

REFRACTORIES

BY

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SECOND EDITION

THIRD IMPRESSION

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REFRACTORIES

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PREFACE TO THE SECOND EDITION

Since the publication of the first edition of this book ten years ago, the new information in the field of refractories has increased so rapidly that a complete revision of the text has become necessary. In particular, our comprehension of the nature of clay, the mechanism of plastic flow, deflocculation of slips, and reactions in firing has demanded an entirely new treatment of these subjects.

Several new chapters have been added. Chapter IV, Some Fundamental Concepts of Matter in the Solid State, prepared by Dr. William Parrish of the Geology Department at Pennsylvania State College, gives clearly and concisely a background on which to build the later applications. Also, in Section IV, five chapters, which should be of particular value to the furnace builder, have been added on the selection and use of refractories.

The author wishes to express his gratitude to the many men in the industry who have so kindly assisted him. Particularly important are the fine photographs of hand molding from Mr. Bradley of the A. P. Green Company, the diagrams of the dry press from Dr. Seil of the E. J. Lavino Company, the drawings of furnaces from Dr. F. A. Harvey of the Harbison-Walker Refractories Company, and much valuable material on insulating refractories and the application of refractories from C. L. Norton, Jr., of the Babcock and Wilcox Company.

The following individuals and organizations have also been of great help in reading portions of the manuscript and supplying information from their files: R. E. Birch, Harbison-Walker Refractories Company; John Chipman, Massachusetts Institute of Technology; F. X. Gilg, Babcock and Wilcox Company; C. R. Hayward, Massachusetts Institute of Technology; R. H. Heilman, Mellon Institute; R. A. Heindl, National Bureau of Standards; Herbert Insley, National Bureau of Standards; A. M. Kohler, Babcock and Wilcox Company; J. D. McCullough,

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F. H. NORTON.

CAMBRIDGE, MASSACHUSETTS,
June, 1942.

PREFACE TO THE FIRST EDITION

This book was written to fulfill the demand for a modern treatise on refractories. In order to keep it within a reasonable size it has been found necessary to deal mainly with the fundamental processes involved in the manufacture and use of refractories. Furthermore, the descriptions of the manufacturing processes have been confined to American practice. The important subject of the proper use of refractories in furnace design and construction has been omitted, since to do it justice a whole volume would be needed. On certain subjects it was found that a great deal of important information was lacking, and the attempt has been made in each case to indicate the direction in which research should be carried to provide the additional data needed for the understanding of the principles involved.

Although a portion of the material contained in this book has been taken from published data, a considerable amount of new material has been included. This has been obtained from the extensive work on refractories carried out in the laboratories of the Babcock & Wilcox Company. Unless otherwise stated, nearly all the experimental data in the book were derived from this source. In all cases the attempt has been made to indicate, by the use of references, where additional information may be obtained on any particular subject.

Chapter XVI was prepared by Prof. J. L. Gillson of the Massachusetts Institute of Technology, whose experience in the examination of clays and ceramic products makes him especially well fitted to write on this subject. Chapter XVII was written by Prof. J. T. Norton of the Massachusetts Institute of Technology, who has been carrying on X-ray studies of crystals for a number of years. Chapter XVIII was prepared by Mr. J. B. Romer, chief chemist of the Babcock & Wilcox Company. Mr. Romer has had many years of experience in analyzing clays and ceramic products.

The author wishes to acknowledge the valuable assistance rendered in the preparation of this book by a large number of

individuals connected with the refractories industry. I am particularly indebted to Mr. Isaac Harter, vice president of the Babcock & Wilcox Company; Prof. C. L. Norton, Prof. G. B. Wilkes, and Prof. C. E. Locke of the Massachusetts Institute of Technology; Mr. A. M. Kohler, Mr. J. E. Brinckerhoff, and Mr. Robert Richardson of the Babcock & Wilcox Company; and Mr. E. B. Powell of Stone & Webster, Inc.

A considerable number of industrial concerns connected with the refractories industry have cooperated most heartily in supplying up-to-date illustrations. Separate acknowledgment has been made in each case.

The numerous photomicrographs throughout the book are due to the painstaking work of C. L. Norton, Jr., who is carrying on research in ceramic petrography at the Massachusetts Institute of Technology, under a Babcock & Wilcox fellowship.

F. H. NORTON.

CAMBRIDGE, MASSACHUSETTS,
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PART I

Introduction

CHAPTER I

SCOPE OF THE REFRACTORIES INDUSTRY IN THE UNITED STATES

1. The Refractories Industry.—Although the manufacture of refractories is not one of the largest industries, it is a particularly important one, as all processes using high temperatures are dependent on it. The refractories industry in the United States

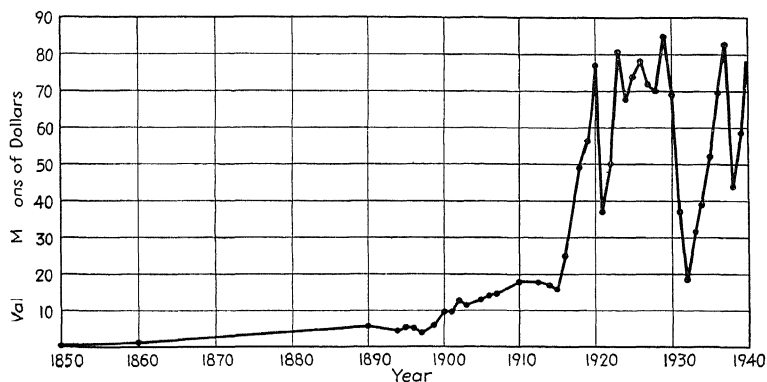


FIG. 1.—Total value of refractories produced in the United States.

has shown a rapid growth since the start of the century, as indicated by the production curve in Fig. 1.

A more detailed picture of the refractories production in this country is shown in Tables 1 to 4, which give the amount and value of various classes of refractories turned out each year. In looking over these tables, it will be noted that the firebrick production reveals a proportional decrease in the last 15 years, due mainly to its displacement by high alumina and insulating

TABLE 1.—REFRACTORIES INDUSTRY STATISTICS—CLAY REFRACTORIES PRODUCTION*
Normal production average based on 1925-1927 = 100

Year	Fireclay bricks				High-alumina bricks				Special shapes (clay refractories)				Total day firebricks			
	Thou- sands	Value	Pro- duc- tion, per- centage	Unit value	Thou- sands	Value	Pro- duc- tion, per- centage	Unit value	Thou- sands	Value	Pro- duc- tion, per- centage	Unit value	Thou- sands	Value	Pro- duc- tion, per- centage	Unit value
Normal	954,765, based on 1925-1927				8,470, based on 1925-1927				50,000, based on 1925-1927				981,791, based on 1925-1927			
1919	Included in total firebrick				Included in total firebrick				Included in other day products				963,339,838,015,732			
1920	Included in total firebrick				Included in total firebrick				Included in other day products				1,114,869,53,415,888			
1921	Included in total firebrick				Included in total firebrick				Included in other day products				621,009,24,833,297			
1922	815,286,830,534,262		85.3	\$37.47	24,138,8		253.1	\$ 37.43	Included in other day products				336,724,31,356,741			
1923	1,105,575,45,370,488		115.7	41.04	28,629,1		338.2	45.50	Included in other day products				1,134,225,46,676,637			
1924	940,948,39,671,315		98.5	42.16	4,541		170.4	65.71	Included in other day products				955,399,40,630,941			
1925	940,113,40,727,678		103.7	41.13	4,541		170.4	65.71	Included in other day products				945,079,41,163,701			
1926	1,007,784,40,013,394		105.5	39.70	9,425		107.3	87.82	Included in other day products				1,034,057,42,706,932			
1927	866,397,34,257,297		90.7	39.57	11,451		134.0	104.58	Included in other day products				915,633,38,173,878			
1928	854,395,33,537,128		89.5	39.22	13,540		163.6	96.42	Included in other day products				893,376,37,301,725			
1929	938,218,36,168,898		98.2	38.55	23,911		282.3	88.44	Included in other day products				1,014,269,43,376,118			
1930	735,984,29,737,369		77.3	40.24	1,533		136.7	134.54	Included in other day products				905,462,36,653,853			
1931	410,041,15,655,507		42.5	37.70	7,190		82.8	104.40	Included in other day products				959,393,19,458,338			
1932	217,242,7,611,372		22.7	35.03	4,844		57.4	95.39	Included in other day products				946,676,9,923,924			
1933	372,523,13,116,020		39.0	35.30	9,353		112.7	75.20	Included in other day products				412,621,16,127,758			
1934	300,214,15,455,175		40.8	39.68	15,719		185.5	65.13	Included in other day products				438,963,19,242,598			
1935	481,679,19,406,800		50.4	40.47	13,229		156.1	81.01	Included in other day products				539,362,23,832,348			
1936	615,498,26,579,073		64.5	43.18	11,151		131.7	98.84	Included in other day products				691,446,32,885,945			
1937	700,947,32,846,495		73.4	40.80	27,559		324.2	77.70	Included in other day products				781,038,39,690,949			
1938	340,153,17,235,535		36.3	49.80	16,495		190.0	107.14	Included in other day products				397,548,31,662,957			
1939	500,570,25,125,128		52.5	49.59	16,799		197.1	90.46	Included in other day products				506,506,30,460,789			

* Table prepared by A. M. Kohler, Babcock and Wilcox Co.

TABLE REFRACTORIES INDUSTRY STATISTICS—NONCLAY REFRACTORIES PRODUCTION
Normal production average based on 1925-1927 = 100

Year	Silica				Magnesite and chrome				Other nonclay includes those of alumina and silicon carbide				Total nonclay refractories			
	Thou- sands	Value	Pro- duc- tion, per- centage	Unit value	Thou- sands	Value	Pro- duc- tion, per- centage	Unit value	Value	Pro- duc- tion, per- centage	Thou- sands	Value	Pro- duc- tion, per- centage	Value	Pro- duc- tion, per- centage	Unit value
Normal	249,389, based on 1925-1927				14,237, based on 1925-1927				\$4,008,511, based on 1925-1927				263,653, based on 1925-1927			
1919	211,120	\$10,911,808	84.8	\$51.63					No data	No data			211,420	\$10,911,898	80.2	\$51.63
1920	230,382	15,076,821	100.5	60.17					No data	No data			230,582	15,076,821	95.1	60.17
1921	169,990	5,220,610	52.5	9.73					\$2,373,299	54.9			109,990	7,753,819	41.7	70.49
1922	186,517	7,353,109	71.8	10.38					3,650,791	80.0			107,116	13,853,396	74.7	70.28
1923	255,388	12,854,007	102.4	9.73					1,913,301	42.2			271,433	18,858,710	103.0	69.47
1924	204,338	10,681,373	81.9	9.73					3,353,112	72.8			217,090	17,273,372	82.4	79.56
1925	235,871	11,290,127	94.6	17.82					3,063,156	66.4			218,609	18,091,155	94.3	72.78
1926	266,801	13,615,033	106.8	51.10					5,083,373	110.3			282,539	23,158,051	107.2	83.02
1927	215,880	12,705,211	98.6	51.88					5,880,003	123.3			250,822	22,311,175	98.6	85.87
1928	211,523	12,187,539	96.8	50.46					5,112,921	118.1			253,639	21,771,286	97.0	85.17
1929	294,102	15,163,260	118.0	51.51					6,980,121	151.7			311,801	27,783,121	118.3	89.11
1930	212,610	11,323,169	88.3	51.19					4,910,292	103.5			226,072	20,311,315	85.8	89.97
1931	103,537	5,151,511	41.5	19.55					4,768,719	103.5			111,922	12,131,075	42.5	116.0
1932	10,111	1,762,110	16.0	13.93					2,916,342	52.4			13,278	5,022,005	16.4	108.4
1933	110,888	4,651,776	44.5	55.10					2,916,342	52.4			111,174	10,181,112	45.5	81.90
1934	103,531	5,705,211	41.5	55.10					2,696,033	58.5			111,174	11,192,850	43.3	100.66
1935	119,621	8,179,990	60.0	54.30					6,396,189	143.1			161,733	18,200,905	61.3	93.99
1936	299,355	12,453,330	91.9	51.30					5,232,533	113.9			219,738	23,173,114	94.7	93.99
1937	290,110	12,802,663	88.3	58.16					8,107,172	175.9			212,868	27,636,778	92.1	113.79
1938	90,952	5,172,512	36.5	60.17					2,839,281	61.6			102,012	11,980,993	39.1	116.36
1939	173,382	9,019,178	82.0	52.02					5,889,913	129.9			191,931	21,112,658	73.9	109.85

* Table prepared by A. M. Kohler, Babcock and Wilcox Co.

TABLE 3.—REFRACATORIES INDUSTRY STATISTICS—CEMENTS AND MORTARS PRODUCTION*
Normal production average based on 1925-1927 = 100

Year	Refractory cements (clay)			Refractory cements (nonclay)			Total refractory cements			Fireclay (raw and prepared)		
	Tons	Value	Pro- duc- tion, per- cent- age	Tons	Value	Pro- duc- tion, per- cent- age	Tons	Value	Pro- duc- tion, per- cent- age	Tons	Value	Pro- duc- tion, per- cent- age
Normal	36,803, based on 1925-1927			50,809, based on 1925-1927			87,330, based on 1925-1927			540,076, based on 1925-1927		
1919	Included in other than clay or silica refractories			Included in other than clay or silica refractories			:					
1920	Included in other than clay or silica refractories			Included in other than clay or silica refractories								
1921	Included in other than clay or silica refractories			Included in other than clay or silica refractories								
1922	Included in total cements			Included in total cements								
1923	Included in total cements			Included in total cements								
1924	Included in total cements			Included in total cements								
1925	32,165.81, 270,000, 57,283.9, 48			46,312.81, 1,000,270, 91.1, 821.50			11,551.1, 252,032, 13.1, 822.00					
1926	31,816.1, 1,328,216, 86.3, 41.74			45,788.1, 1,015,468, 90.1, 22.83			95,812.1, 1,835,349, 110.0, 19.15			768,83, 181,808, 119.9, 84.91		
1927	45,609.1, 2,211,257, 123.7, 27.21			60,328.1, 2,236,126, 118.7, 20.49			27,160.7, 758,989, 31.6, 27.63			2,197,201, 67.3, 6.04		
1928	51,331.1, 932,326, 139.2, 18.16			70,103.1, 1,611,561, 138.0, 23.45			77,601.2, 2,373,684, 89.2, 28.92			3,482,236, 121.6, 5.30		
1929	57,532.1, 1,692,535, 136.1, 29.41			80,892.1, 1,620,773, 139.0, 17.58			105,937.2, 2,177,683, 121.7, 23.38			2,666,813, 88.1, 5.60		
1930	37,912.1, 1,579,590, 102.9, 41.13			60,720.1, 1,116,555, 119.5, 23.32			2,376,880, 139.5, 21.22			2,597,779, 90.2, 5.33		
1931	38,578.1, 1,319,922, 104.6, 34.99			85,611.1, 920,067, 70.1, 25.82			3,113,308, 158.4, 22.50			2,742,020, 93.9, 5.40		
1932	21,766.1, 896,292, 59.0, 39.80			16,693.1, 413,525, 32.8, 26.56			2,196,155, 113.0, 30.36			2,199,952, 85.9, 4.73		
1933	26,375.1, 1,056,503, 71.5, 40.08			42,009.1, 1,300,109, 82.9, 26.36			2,269,980, 84.9, 30.59			2,253,919, 100.3, 4.15		
1934	24,663.1, 1,287,170, 64.9, 51.38			48,853.1, 1,070,122, 80.4, 20.19			1,309,817, 44.0, 84.05			970,121, 39.6, 4.53		
1935	35,044.1, 1,660,118, 97.5, 46.18			88,951.1, 1,903,351, 76.6, 23.20			78.4, 31.93, 192, 138			686,230, 24.9, 5.09		
1936	41,456.1, 1,912,197, 112.5, 46.83			54,918.1, 1,132,556, 108.1, 20.61			2,337,592, 75.0, 35.67			1,012,263, 35.4, 5.26		
1937	57,927.1, 2,467,771, 137.1, 42.00			114,718.1, 2,275,000, 225.6, 19.83			2,363,469, 85.7, 34.23			2,532,670, 1,190,339, 46.9, 5.11		
1938	45,221.1, 2,073,016, 122.7, 45.84			135,051.1, 2,262,201, 265.8, 16.31			4,712,771, 107.7, 27.47			377,344, 1,583,128, 69.9, 4.19		
1939	52,866.1, 2,199,838, 113.4, 47.28			152,141.2, 54,551, 134, 616			4,275,220, 206.4, 23.40			1,681,371, 73.0, 4.27		
							198,275, 47.65			988,307, 36.7, 4.98		

* Table prepared by A. M. Kohler, Babcock and Wilcox Co.

TABLE 4.—REFRACTORIES INDUSTRY STATISTICS—OTHER REFRACTORIES PRODUCTION*
Normal averaged based on 1925-1927 = 100

Year	Glass house refractories			Crucibles		Other clay products		Total	
	Tons	Value	Production, per-centage	Value	Production, percentage	Value	Production, percentage	Value	Production, percentage
Normal		41,177, based on 1927		\$2,751,736, based on 1929		\$6,460,630, based on 1925-1927		\$74,480,583, based on 1925-1927	
1919		Included in firebrick		Included in nonclay refractories		8,840,492	136.8	57,771,182	77.5
1920		Included in firebrick		Included in nonclay refractories		6,981,068	139.0	77,473,777	104.0
1921		Included in firebrick		Included in nonclay refractories		4,586,612	71.0	37,173,758	49.9
1922		Included in firebrick		Included in nonclay refractories		6,345,385	98.2	50,807,909	68.2
1923		Included in firebrick		Included in nonclay refractories		11,185,473	173.1	81,738,067	109.7
1924		Included in firebrick		Included in nonclay refractories		8,111,146	125.5	68,960,739	92.6
1925		Included in firebrick		Included in nonclay refractories		8,561,014	132.5	73,571,376	98.8
1926		Included in firebrick		Included in nonclay refractories		6,585,182	101.9	77,790,692	104.4
1927	41,177	\$2,310,473	100.0	Included in nonclay refractories		4,235,694	65.5	72,106,682	96.8
1928	35,513	1,993,609	86.2	Included in nonclay refractories		3,617,377	55.9	70,095,907	94.1
1929	35,192	2,276,009	85.4	Included in nonclay refractories		4,237,036	65.5	85,739,283	115.1
1930	34,417	1,953,644	83.5	1,700,000	61.7	4,150,053	64.2	69,449,169	93.2
1931	22,853	1,258,546	55.4	1,113,972	40.4	1,584,548	24.5	38,817,937	52.1
1932	15,869	908,285	38.5	639,207	23.2	693,643	10.7	19,204,937	25.9
1933	22,065	1,757,118	53.5	757,996	27.5	745,080	11.5	32,652,077	43.8
1934	25,203	2,375,693	61.2	870,855	30.9	1,293,068	20.0	38,909,396	52.2
1935	27,525	2,441,113	66.8	1,035,644	37.6	3,566,875	55.2	52,830,913	70.9
1936	29,478	2,483,669	71.6	1,880,921	68.4	4,260,877	66.1	69,651,707	93.5
1937	39,392	3,310,077	95.7	1,779,303	64.7	4,203,042	65.1	83,044,491	112.0
1938	22,940	1,942,831	55.7	1,020,761	37.1	2,325,246	36.0	44,232,315	59.4
1939	26,956	2,338,683	65.4	1,666,976	60.9	3,281,974	50.1		

* Table prepared by A. M. Kohler, Babcock and Wilcox Co.

firebrick. The cements and plastics have shown an increase, as in some cases plastic refractories have replaced the usual firebrick construction. The production of silica, magnesite, and chrome brick indicate no definite trends.

2. Refractories in Relation to Other Industries.—Many industries are absolutely dependent upon refractories. For example, the power industry uses great quantities in boiler furnaces, even though the tendency has been in the last few years to employ water-cooled walls in the larger units. The use of plastic chrome refractories to line the water walls has become a very general practice in powdered-coal- and oil-fired boiler furnaces.

The iron and steel industry is vitally concerned with refractories, as evidenced by the large amount of research and development work in this field that is being carried out by the large companies. It may fairly be said that not only the efficiency of the various units producing steel are vitally affected by the properties of the refractories but, in some cases, better qualities of steel could be produced if improved refractories were available.

In the nonferrous industry, refractories also play an essential part, both for withstanding high temperatures and for resisting various types of slag.

Refractories are also of vital importance to many other industries such as the kilns for ceramic production, glass furnaces, linings of rotary kilns for manufacture of Portland cement, incinerators, black-liquor furnaces, and even household oil-burner furnaces.

3. Future Trends in the Industry.—There is a constant demand for refractories of better quality, and the refractory manufacturer is always looking about for new types of raw materials. Materials that may seem rare at the present time will perhaps, in the future, be discovered in large enough quantities to make them commercially available. For example, topaz has been considered a comparatively scarce mineral; but in the South, a massive deposit has recently been discovered having commercial possibilities as a refractory.

In the future, much will be done in the direction of purification of raw materials using the well-established methods of ore dressing applied to the nonmetallic industry. Many fireclays can be materially increased in refractoriness by a simple flotation process to remove iron minerals, and minerals such as kyanite can be

concentrated by ore-dressing methods to give a product of high purity.

New manufacturing methods will undoubtedly be developed for producing refractories of more uniformity and with better physical properties. The firing temperatures will unquestionably be carried higher in the future, and the efficiency of the high-temperature kilns will be increased by new developments in insulation.

Lastly, the refractory manufacturer is becoming more conscious of the particular demands of his customers; consequently refractories will be produced that more nearly fit the individual needs than has been true in the past.

CHAPTER II

LITERATURE ON REFRACTORIES

There is a considerable amount of literature dealing with refractories. Much of it, however, is scattered through books and periodicals, which makes it rather inaccessible to the average reader. It is, therefore, considered advisable to include here some information that will help in finding the published works on refractories.

1. Books.—Probably the most complete book on refractories but somewhat out of date is

SEARLE, A. B.: "Refractory Materials, Their Manufacture and Uses," J. B. Lippincott Company, Philadelphia, 1924.

A number of books deal with the use of refractories. They apply, however, mainly to the steelworking industry. The principal books dealing with the application of refractories are given herewith:

HAVARD, F. T.: "Refractories and Furnaces," McGraw-Hill Book Company, Inc., New York, 1912.

JOHNSON, J. E.: "Blast Furnace Construction in America," McGraw-Hill Book Company, Inc., New York, 1917.

SEARLE, A. B.: "Refractories for Furnaces, Crucibles, etc.," Sir Isaac Pitman & Sons, Ltd., London, 1923.

LINKS, W.: "Industrial Furnaces," John Wiley & Sons, Inc., New York, 1923.

PARTRIDGE, J. H.: "Refractory Blocks for Glass Tank Furnaces," Society of Glass Technology, Sheffield, 1935.

MAWHINNEY, M. H.: "Practical Industrial Furnace Designs," John Wiley & Sons, Inc., New York, 1928.

BUELL, W. C.: "The Open Hearth Furnace" (3 Vols.), Penton Publishing Company, Cleveland, 1936-1937.

KOEPPEL, C.: "Feuerfeste Baustoffe," S. Hirzel, Leipzig, 1938.

There are a number of books concerned in part with raw refractory materials. The book by Ries is the standard work on clays in the United States, and that by Dana is the accepted authority on minerals. Most of the recent work on raw materials will be

found in the U.S. Geological Survey bulletins. The following list comprises the more important books on this subject:

- BISCHOF, C.: "Die Feuerfesten Thone," Quandt, Leipzig, 1904.
 RIES, H.: "Clays, Their Occurrence, Properties and Uses," John Wiley & Sons, Inc., New York, 1908.
 DANA, E. S.: "A System of Mineralogy," John Wiley & Sons, Inc., New York, 1914.
 LEVY, S. I.: "The Rare Earths," Edward Arnold & Co., London, 1915.
 LADOO, R. B.: "Non-metallic Minerals," McGraw-Hill Book Company, Inc., New York, 1925.
 RYSCHKEVITSCH, E.: "Graphite," S. Hirzel, Leipzig, 1926.
 WILSON, H.: "Ceramics-clay Technology," McGraw-Hill Book Company, Inc., New York, 1928.
 BUSS, E.: "Properties of Clay," *Tonind.-Ztg.*, 1928.
 KNIBBS, N. V. S.: "Industrial Uses of Bauxite," Ernest Benn, Ltd., London, 1928.
 BANGO, R.: "Der Magnesit," Steinkopff, Dresden, 1932.
 COMBER, A. W.: "Magnesite as a Refractory," Charles Griffin & Company, Ltd., London.

The manufacture of refractories is treated in a number of books' but little material is available on the most modern manufacturing methods; however, the books listed below give fairly complete descriptions of the past and present methods used in the manufacture of refractories.

- LOVEJOY, E.: "Drying Claywares," T. A. Randall and Company, Inc., Publishers, Indianapolis, 1916.
 GREAVES-WALKER, A. F.: "Clay Plant Construction and Operation," *Brick and Clay Record*, 1919.
 SEARLE, A. B.: "Modern Brick Making," Scott, Greenwood & Sons, London, 1920.
 LOVEJOY, E.: "Burning Claywares," T. A. Randall and Company, Inc., Publishers, Indianapolis, 1922.

A few of the many books that deal in whole or in part with the physics and chemistry of refractories are listed below:

- AUDLEY, J. A.: "Silica and the Silicates," D. Van Nostrand Company, Inc., New York, 1921.
 BINGHAM, E. C.: "Fluidity and Plasticity," McGraw-Hill Book Company, Inc., New York, 1922.
 SEARLE, A. B.: "The Chemistry and Physics of Clays and Other Ceramic Materials," D. Van Nostrand Company, Inc., New York, 1924.
 MELLOR, J. W.: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 6, "Silicates," Longmans, Green and Company, New York, 1926.

International Critical Tables, McGraw-Hill Book Company, Inc., New York, 1927.

SOSMAN, R. B.: "The Properties of Silica," Chemical Catalog Company, Inc., New York, 1927.

BRAGG, W. R.: The Crystalline State, George Bell & Sons, Ltd., London, 1933.

Books concerned with the measurement of high temperature are noted below:

BURGESS, G. K., and H. LE CHATELIER: "The Measurement of High Temperatures," John Wiley & Sons, Inc., New York, 1912.

GRIFFITHS, EZRA: "Methods of Measuring Temperatures," J. B. Lippincott Company, Philadelphia, 1926.

FISHENDEN, M., and O. A. SAUNDERS: "The Calculation of Heat Transmission," His Majesty's Stationery Office, London, 1932.

WOOD, W. P., and J. M. CORK: "Heat Measurements," McGraw-Hill Book Company, Inc., New York, 1927.

ANON.: "Temperature: Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, 1940.

The best available work on the history of refractories in the United States is

RIES, H., and H. LEIGHTON: "The History of the Clay Working Industry in the United States," John Wiley & Sons, Inc., New York, 1909.

There are a number of books dealing with the optical study of crystals, a few of which are noted below:

LARSEN, E. S.: "Microscopic Determination of the Non-opaque Minerals," Government Printing Office, Washington, D.C., 1921.

WINCHELL, N. H., and A. N. WINCHELL: "Elements of Optical Mineralogy," Vols. I, II, III, John Wiley & Sons, Inc., New York, 1927.

WINCHELL, A. N.: "Optic and Microscopic Characters of Artificial Minerals," *Univ. Wis., Studies in Sci.*, 4, 1927.

2. Periodicals and Other Publications.—A great many publications contain information on refractories, but only a few of them are devoted exclusively to refractories. The majority have only occasional articles dealing with this subject. From a scientific and technical point of view the *Journal of the American Ceramic Society* and the *Transactions of the British Ceramic Society* are of the greatest importance. The periodicals in the following list have important or frequent articles on refractories:

American Ceramic Society, *Journal, Bulletin, Abstracts*, Columbus, Ohio.
American Refractories Institute, *Technical Bulletin*, Pittsburgh, Pennsylvania.

American Society for Testing Materials, *Proceedings*, Philadelphia, Pennsylvania.

Berichte der deutschen keramischen Gesellschaft, Berlin-Halensee, Germany.

Brick and Clay Record, Chicago, Illinois.

British Ceramic Society, *Transactions*, Stoke-on-Trent, England.

British Clayworker, London, England.

Ceramic Age, The Ceramic Publishing Co., Newark, New Jersey.

Ceramic Industry, Chicago, Illinois.

Céramique, Paris (10^e), France.

Ogneupory, Russia.

Ohio Ceramic Industries Association, *Bulletins*, Ohio State University, Columbus, Ohio.

Refractories Journal, Sheffield, England.

Sprechsaal, Müller und Schmidt, Coburg, Germany.

U.S. Bureau of Mines, *Bulletins, Circulars, Mineral Resources, Reports of Investigations, Technical Papers*, Washington, D.C.

U.S. Bureau of Standards, *Circulars, Scientific Papers, Technical News Bulletins, Technical Papers, Journal of Research*, Washington, D.C.

The publications in the following list contain occasional references to refractories:

American Chemical Society, *Journal*, Charles L. Parsons, Washington, D.C.
American Electrochemical Society, *Transactions*, Columbia University, New York.

American Foundrymen's Association, *Transactions*, C. E. Hoyt, Chicago, Illinois.

American Glass Review, Commoner Publishing Co., Pittsburgh, Pennsylvania.

American Institute of Chemical Engineering, *Transactions*, Polytechnic Institute, Brooklyn, New York.

American Institute of Mining and Metallurgical Engineers, *Transactions*, Pittsburgh, Pennsylvania.

American Iron and Steel Institute, Yearbook, New York.

American Mineralogist, George Banta Publishing Company, Menasha, Wisconsin.

American Society of Mechanical Engineers, *Transactions*, New York.

American Zinc Institute, *Bulletin*, New York.

Annalen der Physik, J. A. Barth, Leipzig, Germany.

Archiv für Wärmewirtschaft und Dampfkesselwesen, Berlin, N.W. 7, Germany.

Australia Advisory Council of Science and Industry, *Bulletins*, Institute of Science and Industry, East Melbourne, Australia.

Australasian Institute of Mining and Metallurgy, *Proceedings*, Melbourne, Australia.

Blast Furnace and Steel Plant, Steel Publications, Inc., Pittsburgh, Pennsylvania.

Brennstoff- und Wärmewirtschaft, W. Knapp, Halle (Salle), Germany.

British Cast Iron Research Association, *Bulletin*, Central House, Birmingham, England.

- British Geological Survey, *Memoirs*, His Majesty's Stationery Office, London, W.C. 2, England.
- Canadian Chemistry and Metallurgy*, Westmann Press Ltd., Toronto 2, Canada.
- Canadian Institute of Mining and Metallurgy, *Bulletins*, Montreal, Quebec, Canada.
- Céramique et verrerie*, Paris, France.
- Chaleur et industrie*, Paris, France.
- Chemical Engineering and Mining Review*, Tait Publishing Co., Melbourne, Australia.
- Chemical & Metallurgical Engineering, McGraw-Hill Publishing Company, Inc., New York.
- Chemical, Metallurgical and Mining Society of South Africa, *Journal*, H. A. G. Jeffreys, Johannesburg, South Africa.
- Chemie der Erde*, Gustav Fischer, Jena, Germany.
- Combustion*, Combustion Publishing Co., New York.
- Corriere dei ceramisti*, Perugia, Italy.
- Department of Scientific and Industrial Research, *Publications*, His Majesty's Stationery Office, London, W.C. 2, England.
- Economic Geology*, Economic Geology Publishing Co., Urbana, Illinois.
- Engineer*, London, W.C. 2, England.
- Engineering and Boiler House Review*, Engineering Review Company, London, W.C. 1, England.
- Engineering and Mining Journal*, McGraw-Hill Publishing Company, Inc., New York.
- Faraday Society, *Transactions*, Gurney and Jackson, London, England.
- Feuerungstechnik*, Berlin, W. 57, Germany.
- Forging, Stamping, and Heat Treating*, Steel Publications, Inc., Pittsburgh, Pennsylvania.
- The Foundry*, The Penton Publishing Company, Cleveland, Ohio.
- Foundry Trade Journal*, Industrial Newspapers, Ltd., London, W.C. 2, England.
- Franklin Institute Journal*, Philadelphia, Pennsylvania.
- Gas-Age Record*, Robbins Publishing Co., New York.
- Geological Survey of Great Britain*, His Majesty's Stationery Office, London, W.C. 2, England.
- Geological Survey of New South Wales, *Records*, John Spence, Sydney, Australia.
- Glashütte*, Verlag, "Die Glashütte," Dresden, A. 24, Germany.
- Glass*, Glass Publications Ltd., London, W.C. 2, England.
- Glass Industry*, Glass Industry Publishing Co., New York.
- Glastechnische Berichte*, Deutschen glastechnischen Gesellschaft, Frankfurtam-Main, Germany.
- Illinois State Geological Survey*, University of Illinois, Urbana, Illinois.
- Imperial Industrial Research Institute, *Reports*, Department of Commerce and Industry, Osaka, Japan.
- Indian Institute of Science, *Journal*, Bangalore, India.
- Industrial and Engineering Chemistry*, Charles L. Parsons, Washington, D.C.

- Industrie chimique*, H. Mounier, Paris (8°), France.
- Institute of Fuel Technology, *Proceedings*, London, England.
- Institute of Economic Mineralogy and Metallurgy (Moscow), *Transactions*, Scientific-technical Department of Supreme Council of National Economy, Moscow, U.S.S.R.
- Institute of Mechanical Engineers (London), *Proceedings*, London, S.W. 1, England.
- Institute of Physical and Chemical Research, *Bulletin*, *Scientific Papers*, Iwanami Shoten, Tokyo, Japan.
- Iron Age*, New York.
- Iron and Steel of Canada*, Industrial and Educational Publishing Co., Ltd., Gardenvale, Quebec, Canada.
- Iron and Steel Engineer*, Association of Iron and Steel Electrical Engineers, Pittsburgh, Pennsylvania.
- Iron and Steel Industry*, England.
- Journal of Geology*, University of Chicago Press, Chicago, Illinois.
- Kentucky Geological Survey, *Publications*, Frankfort, Kentucky.
- Keramische Rundschau*, Berlin, N.W. 21, Germany.
- Keramos*, Verlag Aktiengesellschaft, Bamberg 3, Germany.
- Kolloid Zeitschrift*, Wolfgang Ostwald, Leipzig, Germany.
- Kolloidchemische Beihefte*, T. Steinkopf, Leipzig, Germany.
- Mechanical Engineering*, The American Society of Mechanical Engineers, New York.
- Metal Progress*, American Society for Metals, Cleveland, Ohio.
- Mining Journal*, London, E.C. 4, England.
- Mining and Metallurgy*, American Institute of Mining and Metallurgical Engineers, Inc., New York.
- National Academy of Sciences, *Proceedings*, Washington, D.C.
- Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie*, Stuttgart, Germany.
- New Zealand Journal of Science and Technology*, Wellington, New Zealand.
- Ohio State University Engineering Experiment Station, *Bulletins*, Ohio State University, Columbus, Ohio.
- Pit and Quarry*, Chicago, Illinois.
- Revue générale des colloïdes et de leurs applications industrielles*, Paris (6°), France.
- Revue de métallurgie*, Paris (9°), France.
- Revue universelle des mines*, Comité scientifique de l'association des ingénieurs, Liège, Belgium.
- Rock Products*, Trade Press Publishing Corporation, Chicago, Illinois.
- Schweizerische mineralogische und petrographische Mitteilungen*, Leeman and Co., A. G. Zurich, Switzerland.
- Science Abstracts*, London, S.W. 1, England, also Spon & Chamberlain, New York.
- Société géologique de Belgique, *Annales*, Liège, Belgium.
- Société russe de minéralogie, *Annales*, Leningrad, U.S.S.R.
- Soil Science*, The Williams & Wilkins Company, Baltimore, Maryland.
- Stahl und Eisen*, Verlag Stahl Eisen, Düsseldorf, Germany.

- Tôhoku Imperial University, *Scientific Reports*, Maruzen Company, Ltd., Tokyo, Japan.
- U.S. Department of Agriculture, *Bulletins*, Government Printing Office, Washington, D.C.
- U.S. Geological Survey, *Bulletins*, Government Printing Office, Washington, D.C.
- University of Illinois Engineering Experiment Station, *Bulletins*, University of Illinois, Urbana, Illinois.
- University of Toronto, *Monthly*, Toronto, Canada.
- University of Wisconsin, *Studies in Science*, Madison, Wisconsin.
- Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, Verlag Chemie, Leipzig, Germany.
- Zeitschrift für Kristallographie*, Akademische Verlagsgesellschaft, Leipzig, Germany.
- Zeitschrift für Physik*, Verlag Julius Springer, Berlin, W. 9, Germany.

3. Bibliographies.—There are a number of excellent bibliographies covering the complete ceramic field as well as limited portions of it pertaining directly to refractories. The following bibliographies cover the complete field of ceramics quite thoroughly up to the time of their publication. M. L. Solon gives us critical abstracts of most of the books and also an excellent classification. However, he writes mainly from the point of view of the artist, and the number of references of value on modern refractories is limited.

- BRANNER, J. C.: "A Bibliography of Clays and the Ceramic Arts," American Ceramic Society, Columbus, Ohio, 1906. Covers whole ceramic field up to 1906.
- SOLON, M. L.: "A Bibliography on Ceramic Literature." Charles Griffin & Company, Ltd., London, 1910. Critical abstracts are given of most of the books. Well classified.

In the following list are included a number of up-to-date bibliographies dealing with special refractory divisions, which will be found of more direct value than the preceding list.

- McDOWELL, J. S., and H. S. ROBERTSON: "Bibliography of Chrome Refractories," *J. Am. Ceram. Soc.*, Vol. 5, p. 865, 1922. Covers this field up to 1922.
- ANON.: "Bibliography of Magnesite Refractories," American Ceramic Society, 1924. Covers this field up to 1922.
- ANON.: "Bibliography of Silica Refractories," American Ceramic Society, 1924. Covers this field up to 1922.
- ANON.: Literature on Refractories for the Glass Industry, *Glass Ind.*, Vol. 7, 11, pp. 275-276, 1926.

- NORTON, F. H.: Bibliography on Thermal Conductivity of Refractories, *J. Am. Ceram. Soc.*, Vol. 10, p. 30, 1927. Up to 1927.
- ANON.: Bibliography of Literature on Refractories, *J. Am. Ceram. Soc.*, Vol. 10, p. 2, 1927.
- FERGUSON, R. F.: Review of the Literature on Laboratory Slag Tests for Refractories, *J. Am. Ceram. Soc.*, Vol. 11, pp. 90-99, 1928.
- COHN, W. M.: Bibliography of Heat Effects on Ceramic Materials, *J. Am. Ceram. Soc.*, Vol. 11, p. 296, 1928. From 1919 to part of 1928.
- LITINSKY, L.: Bibliography on Refractory Materials for Iron and Steel Works, *Feuerfest*, Vol. 4, 2, pp. 30-32, 1928.
- McVAY, T. N.: Bibliography of Ceramic Microscopy, *Bull. Am. Ceram. Soc.*, Vol. 16, p. 33, 1937.
- MARDEN, J. W. and M. N. RICH: Bibliography on Zirconium and Its Compounds, *Bur. Mines, Bull.* 186.

4. Abstracts.—The most complete abstracts of the literature on refractories are found in the *Journal of the American Ceramic Society*. The *Transactions of the British Ceramic Society* also has a fairly complete list of abstracts taken from the more important publications. In *Science Abstracts* and *Chemical Abstracts* will be found quite a few references to the more scientific and technical phases of this subject.

Throughout this book at the end of each chapter have been placed the more important references and publications dealing with the subject of that particular chapter. The selection of these references was somewhat difficult because of the tremendous mass of available material. However, the choice was guided by the amount of original data included in the reference and its accessibility in the average library. Also the more recent articles were considered in place of the early ones except where an early article was a particularly valuable or original contribution to the subject.

CHAPTER III

HISTORY OF REFRACTORY DEVELOPMENT IN THE UNITED STATES

The early history of refractories in the United States is shrouded in considerable obscurity. A number of references are given here that throw new light on the subject, but a tremendous field still remains to be explored. A few months spent in examining old publications and records of Boston, Baltimore, Philadelphia, and parts of New Jersey would certainly yield valuable information. A little archaeological study around the sites of old furnaces, kilns, and plants would surely produce specimens of the old refractories used.

1. Furnace Stone.—Undoubtedly the earliest type of refractory used in this country was mica schist or siliceous rock. All the early iron furnaces or forges were constructed mainly of this material. Thus we must study the early history of the iron industry. Fortunately this is quite well known, for an iron furnace was much more likely to be a subject of comment than a brickyard. The first furnaces were built in Virginia, but it is quite certain that they were never completed. The first successful furnace was built in 1645 at Saugus, Massachusetts, and the next year another was operated at Braintree. They were probably made from local stone, although there are no very satisfactory deposits in this region. The building of furnaces and forges spread rapidly in the next hundred years, and considerable stone must have been quarried. Samuel Robinson^{(1)*} in 1825 states that furnace stone was quarried near Providence, Rhode Island, for forty or fifty years and carried long distances in wagons for use in furnace hearths. There were probably other famous quarries at this time.

Stone was used for the building of furnaces and forges late into the nineteenth century because of the greater cost of firebrick. Even now, stone is used for lining Bessemer converters. A

* Numbers thus set in parentheses refer to the bibliographies appearing at the end of each chapter.

number of the old stone or stone and brick furnaces are still standing in various parts of the country. Two interesting ones stand on Furnace Brook in Bennington, Vermont, one of which is shown in Fig. 2.

Records⁽¹⁷⁾ show that sandstone was used for the walls of kilns burning refractories. Probably many of the early glass furnaces were built of stone. In fact Robert Hewes of the Temple Glass Company, Temple, New Hampshire, states in a letter dated 1781: "I shall have to send sixty miles for stones to



FIG. 2.—An old iron furnace standing in Bennington, Vermont.

build my melting furnace, which will take eight teams." It is believed that these stones came from Uxbridge, Massachusetts, which is about sixty miles from Temple. Samples from the old furnaces confirm this.

2. Glass Pots and Crucibles.—Probably the first clay refractories used in this country were glass pots. J. B. Felt⁽⁶⁾ in his "Annals of Salem" in 1827 mentions a glass factory in Salem, Massachusetts, in 1638, and again as producing in 1641. The only other information I have been able to obtain is the names of John and Ananias Conklin as glass blowers. All else seems to be lost in the obscurity of time. We may be sure, however, that glass pots were used. They were probably made from English or German clays as were all the early glass refractories.

A century later, the Wister glassworks were started in New Jersey. Gross Almerode or Klingenberg clay was used for the

pots at first, but later New Jersey or Maryland clays were probably used to some extent. J. C. Booth⁽⁴⁾ in 1841 states that a white, highly plastic clay was wrought only in one place, on the Delaware shore below New Castle, and exported for crucibles and glass pots. The clay had been wrought for manufacturing purposes for some forty years. Porcelain crucibles were made of kaolin from New Milford, Connecticut, by a goldsmith in about 1807.

A number of other early glass plants were operated in this country, mainly by Germans. We have the Germantown factory (Braintree, Massachusetts) and the factory of Baron Steigel in 1763, as well as a number of others. German pot clays were probably extensively used, as they are even now. In fact, J. F. Amelung, who started a glassworks at Frederick, Maryland, in 1784, brought over pot makers and built a pot works in conjunction with his plant.

A note in the Gaffield Collection at the Massachusetts Institute of Technology library states that the Boston Crown Glass Company, which for a number of years had been using imported clays for pots, attempted between 1810 and 1812 to replace them with domestic (probably New Jersey) clays. The attempt was not successful.

A recipe book of the Boston Glass Mfg. Co. in the Boston Athenaeum Library has an item dated 1791 that states that 200 lumps of clay were received from Amsterdam, undoubtedly for making pots. Another item lists fuel for keeping the glass pots (green) from freezing.

The manufacture of glass pots as an industry separate from the glass plants was started in 1860 by Thomas Coffin in Pittsburgh.⁽⁹⁾ In 1879, the Pittsburgh Clay Pot Company was organized, and after this many other concerns started in Pennsylvania and Ohio.

3. Lime.—Lime, often made from shells gathered on the shore, was used in forge walls from very early times. There are references to a number of early lime kilns.

4. Fireclay Bricks.—We are still in doubt as to the location of the first American firebrick manufacturer. It may have been New Jersey, Boston, or Baltimore.

New England.—Owing to the early development of iron and glass manufacture here, it is to be expected that firebrick would be

needed at an early date. Stourbridge firebricks (English) are known to have been imported to some extent, but bricks were also made from New Jersey clay. The recipe book of the Boston Glass Mfg. Co. states that in 1790, two helpers were paid to make furnace tile and, in 1791, two men were paid for burning brick for the glass furnace. In 1793, an item lists the payment of expenses for a man to go to New York to procure clay from South Amboy. This is undoubtedly the earliest direct reference to the manufacture of firebrick from native clay. According to Professor Rogers,⁽¹⁸⁾ Mr. G. W. Price of New Brunswick, New Jersey, stated that his father carried a vessel load of fireclay from Woodbridge to Boston in 1816 for use in making firebricks. It was thought to be the first shipment for this use. An advertisement in the *Boston Commercial Gazette* of July 6, 1818, by the New England Glass Company, read, "Also—Fire Brick Clay, raw and prepared, constantly for sale." This would seem to indicate that firebricks were then being made in Boston. In 1820, Jacob Felt of Boston bought 50 tons of clay of Jeremiah Dully, and this was afterward sent regularly from Amboy. Firebricks were made in Boston at this time.

The following advertisement appeared in the *Boston Commercial Gazette* of Mar. 5, 1827. "_____fire bricks made to all dimensions. For sale by Deming Jarves, No. 88 Water St." (New England Glass Bottle Works.) This probably explains where at least part of the New Jersey clay was used.

In 1835, a patent was taken out by Joseph Putnam of Salem for firebricks and stove linings. We do not know whether or not he manufactured, but it is doubtful if he would have applied for a patent for this type of article without having previously made it. As early as 1829, L. Hine used the kaolin of New Milford, Connecticut, for firebricks and furnace linings.⁽³⁾ He evidently had a considerable business; as \$6,000 per year is mentioned as the value of his product, and six workmen were employed. The bricks sold for two-thirds the price of the Stourbridge firebricks and were considered nearly as good.

In 1839, Hiram Harwood of Bennington, Vermont, records in his diary,⁽¹⁵⁾ "Visited works of Judge L. Norton—large low buildings in forwardness for drying newly invented fire bricks—erected N. old works." This business apparently prospered in the next few years and was carried on by Norton and Fenton.

It is quite possible that the manufacture of these bricks was started from information obtained from the New Milford enterprise. We are fortunate in having an accurate account of the manufacture of these early bricks by Norton and Fenton. C. B. Adams, state geologist of Vermont, in his first *Annual Report* (1845), page 52, states:

For firebrick, the kaolin is made into paste with water, from which bricks are formed and burnt. These bricks, retaining the whiteness of the kaolin, and becoming very hard, are called "clay bricks." They are next broken up by a mill and sifted, so as to be of the coarseness of fine gravel. This is mixed with unburnt kaolin and arenaceous quartz, pressed in moulds of the required form and size, and burnt in the same manner as before. These firebricks are very white and hard, and when fractured shew their composition of broken claybrick and kaolin.

C. W. Fenton, in a letter to Mr. Adams at this time, gives more particulars:

The character of our fire-bricks is also well known. They are a composition of materials which we find here, consisting of arenaceous quartz and kaolin. Being very pure, they make a good fire-brick, which will stand longer in a strong heat than any other brick known. They are used for blast furnace hearths, and in many places, where no other fire-bricks will endure.

The value of pottery and firebrick produced then was stated as \$20,000 per year.

In 1841 (Feb. 27), the following advertisement appeared in the *State Banner* of Bennington, Vermont:

Bennington
Stoneware Factory
Julius Norton
Manufactures and keeps constantly for sale

Also *Patent Fire Brick*
(the best in the world) at \$50 per thousand

These kaolin bricks were made in Bennington as late as 1855 or 1856 and had a very general sale as a good firebrick. But owing to the lack of coal and the need of twice burning the highly shrinkable kaolin, they could not long compete in cost with bricks of New Jersey and Pennsylvania.

It is also stated that firebrick of kaolin, New Jersey fireclay, crushed brick and sandstone from Willsboro, New York were

made at Monkton, Vermont, in 1846. These bricks were undoubtedly used in the many charcoal iron furnaces operating in this region, although a large part of the lining was quartzite or mica schist. A reddish firebrick taken from an old furnace standing on Furnace Brook in Bennington, Vermont, fulfills this description quite well. I was also fortunate in finding at the site of the United States Pottery in Bennington a white brick made of coarse calcined grog bonded with kaolin. This brick is marked:

Fire Brick Co's.

No. 1

Bennington, Vt.

Considerable space is given to these early kaolin bricks because we have a fairly complete account of their manufacture and because they are the first to utilize successfully the pure and refractory but high-shrinking kaolin by the method of double burning. For their time, they were really remarkable bricks and have scarcely been mentioned in histories of refractories.

Firebricks and retorts were probably being made in Boston regularly before 1850. In 1864, the Boston Fire Brick and Clay Retort Manufacturing Company was making bricks and retorts on the site of the present South Station. New Jersey fireclay was brought to their own dock. For some years at about this time, the Morton Fire Brick Plant on K Street at South Boston was in operation. Apparently no firebrick has been made in Boston since 1895.

From the beginning of the nineteenth century, a number of stoneware potteries were operating in New England. In every case, firebrick must have been used in their kilns. It is reasonable to suppose that the bricks were made from stoneware clay, all of which at that time came from New Jersey.

The manufacture of stove linings and firebricks has been carried on at Taunton, Massachusetts, for many years. Now Pennsylvania clays are mainly used.

New Jersey.—A stoneware pottery was operated by Coxé at Burlington, New Jersey, in 1684. He probably used English firebrick for his kilns, but some local clay may have been used.

Professor Rogers⁽¹⁸⁾ states that New Jersey clays were used for making firebricks soon after 1812. We need not necessarily assume, however, that the bricks were made in New Jersey.

The clay may have been taken to Boston or Baltimore. In 1825, a firebrick plant (Salamanda Works) was started at Woodbridge, New Jersey. In 1836, John R. Watson established a factory for making firebricks at Perth Amboy. From 1845 to 1865, a number of plants were started in the Woodbridge district, and most of them are still operating. Sayer and Fisher, Henry Maurer & Son, and Valentine & Bro. are well-known firebrick manufacturers at the present day.

Delaware and Maryland.—In a report⁽²⁾ on the state of Maryland, published in 1834, occurs a most significant statement:

Fire brick so far exclusively made in the United States at Baltimore, has been pronounced by competent judges after repeated trials, to be fully equal, if not superior to the far-famed Stourbridge brick of the same nature.

Later it stated that these bricks were used in iron furnaces to replace silica stone.

We may judge from this statement that a high-grade firebrick of the "same nature" as the well-known Stourbridge firebrick was an established industry in Baltimore at this time. The reference to repeated trials would indicate its use for a considerable number of years previous. The statement that firebricks were made only in Baltimore at this time is perhaps founded on lack of knowledge of the industry in New Jersey and Boston but more probably refers to a time some years prior to this date when the Baltimore industry was started. Further investigation is greatly needed on this point.

As previously mentioned,⁽⁴⁾ considerable white refractory clay was mined in Delaware mainly for crucible and glass pots, but some may well have served for bricks.

In 1837, the famous Mt. Savage fireclay was discovered, and the Union Mining Company soon began operations here.

Florida.—Ries⁽⁹⁾ states that records show a shipment of firebrick from Florida to New Orleans in 1827. No more is known of it.

Ohio.—According to Stout,⁽¹⁷⁾ firebricks were first made in Ohio during 1841 by Andrew Russell near East Liverpool. They were produced there continuously until about 1900 by Russell and later by N. U. Walker. The clay mined behind the plant was plastic and of medium refractoriness. In 1852, G. and M.

Meyers started a firebrick plant near Toronto. A plastic, lower Kittanning clay was used.

The manufacture of firebricks from flint clay was begun during 1863 in Scioto County by Reese Thomas. This brick was a high-grade product, made in updraft kilns with sandstone walls.

During 1866, the Diamond Fire Brick Company was opened in Akron by J. P. Alexander. At about the same time, a three-kiln plant was built at Dover. The Federal Clay Products Company and a number of other plants started about 1872 in this district. J. R. Thomas founded the Niles Fire Brick Company at Niles in 1872.

The Oak Hill Fire Brick Company and Actna Fire Brick Company started in the Oak Hill district about 1873. Other plants were opened here later.

Pennsylvania.—It has generally been believed that the first firebricks were made in Pennsylvania about 1836 at Queens Run. However, the following advertising card⁽¹⁹⁾ would indicate that they were made in Philadelphia before 1832.

American China Manufactory
S. W. Corner of Schuylkill Sixth & Chestnut Sts.,
or at the Depository

Where is constantly kept on hand,.....

.....

also offered for sale
Fire-brick & Tile

Of a superior quality, manufactured in part from the materials of which china is composed.—These have been proved, by competent judges, to be equal to the best Stourbridge Brick.

Eight years later the following advertisement⁽¹⁹⁾ appeared.

Abraham Miller
has removed his manufactory
From Zane Street to James, near Broad Street,
Spring Garden

where his works are now in full operation, conducted by his late Foreman, Mr. C. J. Boulter.

.
.
.

A large Assortment of Portable Furnaces, Stove Cylinders, Fire Bricks and Slabs,.....

.....

Philad'a December 22d 1840.

In 1842, James Glover started the manufacture of refractories at Bolivar. The clay is of good quality, and refractories are still made there. In 1845, Kier Brothers started to manufacture at Salina. In 1859, Soisson and Company began manufacturing at Connellsville; and in 1865, the Star Fire Brick Works were built at Pittsburgh.

After this, so many firebrick plants were opened in the state that it assumed the leading position in the manufacture of refractories. The factors contributing to this great development were the excellent deposits of clay, especially flint clay; the abundance of coal; and the ease of distribution.

Missouri.—In the year 1846, the excellent clay deposits of the St. Louis district were opened up. In 1851, the Christy Fire Clay Company was started; and in 1855, both the Evans and Howard and the Laclede Fire Brick Company followed. The St. Louis district was one of the largest producing centers at this time.

Kentucky.—This district was not opened up until about 1871, when fireclay from Lewis County was sent to Cincinnati. In 1884, the clays at Amanda Furnace and Bellport Furnace were worked. Two years later the Ashland Fire Brick Company was started at Ashland.

West Virginia.—Firebricks were not produced in this state until 1876, when the clays of Marion County were worked.

Colorado.—The first firebricks made in this state were manufactured at Golden during 1866. Later clay deposits were opened up at Pueblo and Canon City and now have a good reputation in the west.

The West Coast.—Refractory manufacture was rather late in developing here, but recently many excellent refractories are being made in both California and Washington.

5. Silica Refractories.—Probably the first silica bricks made in the United States were manufactured by J. P. Alexander of Akron, Ohio, about 1866. J. R. Thomas made silica brick for the steel industry at Niles, Ohio, about 1872. He used quartz pebbles and a Sharon conglomerate and called the bricks "Dinas Silica," as they were similar to the European brick of that name. A. Hall of Perth Amboy made some silica bricks in 1875, but apparently there was no great demand for them. The modern silica brick of lime-bonded ganister is a more recent develop-

ment. In the year 1899, the first silica-brick plant was started at Mt. Union, which later became a great center. Silica bricks were made later in the Chicago district.⁽²⁰⁾

6. Chrome Refractories.—Chromite, mainly in the form of bricks, began to be used by the steel manufacturers about 1896, chiefly as a neutral zone between the acid and basic courses. Only a few firms have been manufacturing chrome bricks.

7. Magnesite Refractories.—Magnesite as a steel-furnace lining was suggested in Europe as early as 1860 but did not come into regular use until 1880, when it was found that the Austrian material could be fritted down into a good bottom. Styrian magnesite was imported into this country in 1885 and was used by the Otis Steel Company in the first open-hearth steel plant in the United States. However, it was not a commercial success. In 1888, magnesite was used successfully by Carnegie, Phipps & Co. at Homestead. From this time, the use of magnesite increased rapidly because the general advantages of the basic process over the acid process became evident to all.

In the year 1898, 16,000 tons of Austrian dead-burned grain were imported. Bricks were at first imported, but later they were made in this country by a few companies.

8. High-alumina Refractories.—The first bauxite discovered in the United States was found near Rome, Georgia, during 1888.⁽¹¹⁾ The Arkansas bauxite deposits were discovered in 1891. The production from the latter source increased rapidly, until now it supplies a considerable part of the domestic demand. Coastal bauxite of Georgia was discovered and described in 1909. A number of small deposits are now being worked.

Missouri diasporite was recognized in 1917 as a source of material for super refractories. This discovery has made Missouri one of the most important producing states.

The importation of gibbsite from Dutch Guiana in the last few years has supplied a very high-grade material to the manufacturers of refractories.

The deposits of sedimentary kaolin on the southern coastal plain have been known from the time of the first settlers. The remarkable beds form probably the largest supply of uniform and pure high-grade clay in the world. The suitability of kaolin for refractories was known as early as 1837 in Bennington, but the southern kaolin is of a purer grade and possesses a high

vitrifying point and a very large shrinkage. These properties for many years have prevented its use in a refractory. In the last few years, however, it has been possible to manufacture a successful refractory out of this pure kaolin.

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CHAPTER IV

SOME FUNDAMENTAL CONCEPTS OF MATTER IN THE SOLID STATE

1. Introduction.—The following chapter has been prepared to give in the briefest possible space a view of our modern concepts of matter in the solid state. It is, of course, impractical in the space available more than to outline this subject, but the author feels that the remainder of the chapters cannot be soundly constructed without the firm foundation presented here. It is hoped that the readers will see many illustrations that will explain by the principles of crystal chemistry the underlying cause of various phenomena occurring in the refractories industry. Those wishing to go further than this brief outline should consult the bibliography referred to throughout the chapter.

The Crystalline and the Glassy States.—All solids, either inorganic or organic, may be divided into two major groups on the basis of their atomic arrangement: the crystalline state and the glassy state. The essential difference between them is that in the crystalline state, the atoms are arranged in a symmetrical, periodic network whereas in glasses, the atoms are arranged in a nonsymmetrical, nonperiodic, random network. It is this absence of periodicity, symmetry, and regular continuity in the arrangement of the atoms that gives glasses their nonvectorial properties. The atoms in glasses are held together by bonds of all varieties of strengths, and consequently glasses soften gradually when heated and have no sharp melting point. Of course, the atomic bonding strength in crystals is not uniform throughout the crystal, but there is a considerable proportion of the bonds of exactly equal strengths. Hence many crystals have a relatively sharp melting point. The symmetry of the atomic arrangement in crystals and the periodic repetition of the same atomic motif at regular intervals result in vectorial properties (*i.e.*, variation of properties with crystallographic direction) in the crystalline state. X-ray powder pictures of crystalline materials consist of a number of sharp rings, but glasses produce only a few broad, diffuse rings.

A fundamental law of nature is that all matter tends to reach equilibrium with its environment. To accomplish this, the atoms try to arrange themselves in a structure having the minimum free energy for that particular compound; and, at ordinary temperatures, the structure is usually an ordered crystalline arrangement. In the solid state, this tendency manifests itself in the formation of crystals that are most in "harmony" with their physicochemical environment, chemical composition, and mode of formation. We may generalize and say that a glassy structure, at ordinary temperatures, is the metastable phase and that, even though it may exist for an almost indefinite period of time, it may eventually be converted to the crystalline arrangement, which is the stable phase. Since the glassy state is uncommon in nature, natural minerals with a glassy or amorphous structure form only an insignificant percentage of the earth's crust. Glass can be produced in the laboratory or factory under special conditions, and the tendency for its formation varies, depending on the chemical composition of the melt, the rate of cooling, and the presence of mineralizers. The glassy phase plays an important role in the manufacture and use of refractories especially as a cement to hold particles together on firing and thus to give mechanical strength. On the other hand, too much or too fluid glass will reduce the high-temperature strength, as discussed in Chap. XIII. Some of the properties of the crystalline solids will next be considered.

Crystals.—Because most matter in the solid state is crystalline, a knowledge of crystallography is a necessary prelude to the study of solids. In this section, a few of the fundamental aspects of crystallography will be briefly reviewed. The reader may refer to the books listed in the bibliography at the end of the chapter for more detailed discussions of this topic.

The most obvious characteristic of crystals that have grown freely is their external form. The geometrical study of the mutual relationships of the faces of crystals is known as "morphological crystallography," and for over one hundred and fifty years crystallographers were mainly interested in and devoted most of their attention to this type of investigation. As a result, thousands of crystals were measured and the data were used for purposes of description and identification.⁽²²⁾ The principal fact to emerge from this welter of data was that, regard-

less of the amount of malformation of the crystal and apparent lack of symmetry, all crystals could be classified in one of a limited number of classes based upon their symmetry. The slopes of the faces and the interfacial angles of crystals of the same compound measured at the same temperature are always the same, regardless of the shape of the crystal or the relative sizes of the faces (*Steno's law*, 1669), as shown in Fig. 3 and the illustrations in the section on crystal growth. Moreover, careful measurements showed that the indices (intersections of face with the crystallographic axes) of most faces of the crystal could be represented by small whole numbers (*law of rational indices*). These observations led to speculation on the general architecture

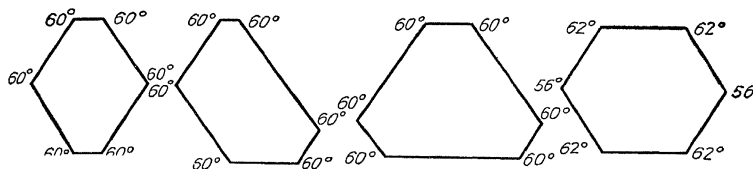


FIG. 3.—Steno's law. Regardless of the sizes of the faces, interfacial angles between similar faces of the same substance are the same when measured at the same temperature. (A. F. Rogers.)

and ultimate building blocks of crystals; but not until the year 1912, with the discovery of X-ray diffraction by crystals was the orderly, systematic arrangement of atoms in the crystalline state proved experimentally. Since that time, interest has swung toward the more fundamental internal symmetry (atomic arrangements), because the external symmetry is but one manifestation of the crystal structure.

A piece of glass cut in the shape of a quartz crystal remains glass, for it has no vectorial properties. Because the atoms have a regular periodic arrangement, a piece of quartz without plain faces is still a crystal and hence has vectorial properties. In other words, the absence of faces from a crystal does not prove the absence of crystallinity. The fundamental feature that differentiates the glassy from the crystalline state is the atomic arrangement. It is the absence of symmetry and periodicity in the glassy state that distinguishes it from the crystalline state. The external crystal form is a relatively minor feature of the crystal and is influenced by many factors, as will be seen in a later section on crystal growth

X-ray diffraction studies show that the atoms in crystals are arranged in an orderly, systematic manner and that the atomic motif is repeated at regular intervals. This orderly atomic arrangement determines the physical and chemical properties of crystalline compounds; hence it is the most fundamental feature of the crystal. The atomic arrangement may be determined by X-ray diffraction studies, and the correlation of crystal structure with properties has developed into the important field of crystal chemistry.

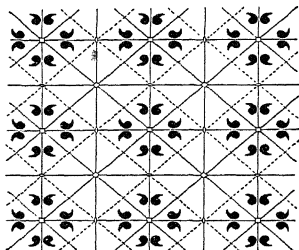


FIG. 4.—Two-dimensional pattern. The black commas represent the motif and lighter lines are the symmetry elements. (Buerger and Lukesh, courtesy of Technology Review.)

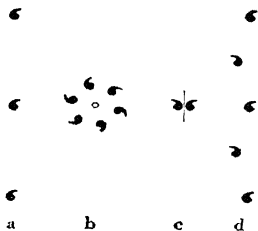


FIG. 5.—Symmetry operations. (a) Translation; (b) sixfold rotor; (c) reflection; (d) glide reflection. (Buerger and Lukesh, courtesy of Technology Review.)

The *motif* may be a single atom, a group of atoms, or a molecule, depending upon the chemical composition and structure of the crystal. Crystals may therefore be treated as three-dimensional *patterns*. The fundamental feature of such patterns is that they are based on certain symmetry operations and only a limited number of unique types are possible. In two-dimensional patterns such as wallpaper or tile designs, 17 types are possible (*plane groups*); and in three-dimensional patterns such as crystals, 230 unique types are possible (*space groups*). Thus the motif may be simple or very complex, but there are a restricted number of ways in which it can be repeated in a plane or in a crystal. A typical two-dimensional pattern is shown in Fig. 4 with commas representing the motif. The solid lines represent reflection lines; dashed lines are glide lines; the small squares are fourfold rotors; and the small ellipses are twofold rotors. A single comma placed in this group of symmetry operations is developed kaleidoscopically into the pattern of commas.

The *symmetry operations* (Fig. 5) are as follows:

Rotors or Axes: These repeat a motif two, three, four, or six times about a point in a plane. Fivefold rotors, so common in biology, and seven-, eight- and higher fold rotors are not used in crystallography.

Reflection: This operation acts like a mirror, making one half of the pattern or crystal look like the other half.

Center or Center of Inversion: This point causes every point or plane in the crystal to have a similar point or plane on the opposite side of the crystal, both being equidistant from the center (Fig. 6).

Rotary Reflection: The term means a combination of a four- or sixfold rotor and a reflection.

Rotary Inversion: This implies combination of a sixfold rotor and a center.

Translations: They extend the pattern in all three dimensions; the translation along parallel directions of the crystal are the same, and the unit translation in a given direction is characteristic of the compound. Its value lies in its use for identification purposes.

Glide Plane: This is a combination of reflection and a half-unit translation.

Screw Axis: This is a combination of two-, three-, four-, or sixfold rotor and translation of one-half, one-third, one-fourth, or one-sixth the unit translation; it may be right- or left-handed.

Various combinations of symmetry operations are possible; and if all are combined in a systematic manner, 230 unique space groups, or collections of symmetry elements, are derived. Certain combinations of symmetry operations automatically introduce other symmetry operations; e.g., the combination of a fourfold rotor and a reflection plane normal to the rotor necessarily forms a center of symmetry at their intersection. It is interesting to note that the space groups were derived some years before their actual existence in crystals was proved experimentally. In the International Tables for Determination of Crystal Structures⁽⁶⁵⁾ are drawings showing the positions of the symmetry elements and their mathematical relations in the 230 space groups.

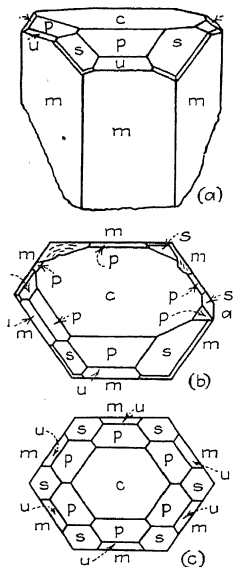


FIG. 6.—(a) and (b) Oblique and top views of a natural crystal of beryl; (c) idealized drawing of the top view of the same crystal showing six planes, a center, and a sixfold axis of symmetry. (L. J. Spencer, "A Key to Precious Stones"; Blackie & Son, Ltd., Glasgow.)

We may better understand crystal patterns by considering the simpler two-dimensional patterns such as textiles or wallpaper. Figure 7 shows a two-dimensional pattern in which each dot representing the motif is repeated at regular intervals. The portion of the pattern outlined by the heavy solid line is the *unit cell*, i.e., the smallest portion that contains a complete unit of the pattern. If we made a rubber stamp of the unit cell and stamped it at all the translation units, we should develop the extended pattern. The dotted lines outline an alternative

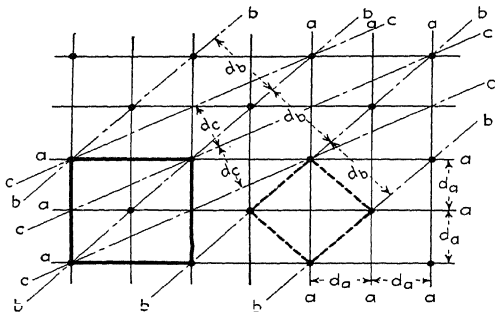


FIG. 7.—A two-dimensional lattice with two possible unit cells. Planes *a* and *b* have a greater chance of appearing as faces on the crystal than planes *c* because they are closer packed. d_a , d_b , and d_c correspond to spacings between different planes which would show up as three different lines on an X-ray powder film.

diamond-shaped unit cell even smaller than the face-centered cell. The choice of the unit cell is somewhat arbitrary, but the crystallographer usually chooses the one that has the smallest axes, is the simplest, and best conforms to symmetry requirements. In this case, we have chosen the unit cell parallel to the principal lattice lines.

The unit cells are stacked together, forming throughout the pattern a continuous network, which is shown by the lighter solid lines. In two dimensions such a network is called the "lattice net" and, in three dimensions, the "space lattice." Thus the space lattice of a crystal is the network of points outlining the repeat period in three dimensions, and it serves as the coordinate system to which the pattern may be referred. Figure 8 shows the 14 space lattices, derived many years ago by Bravais. Although the choice of the unit cell at times may be arbitrary,

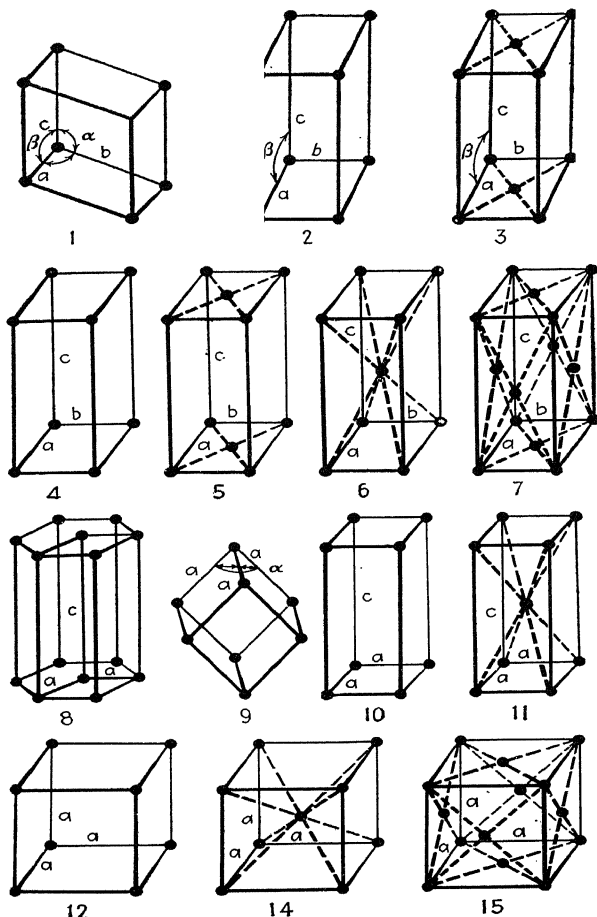


FIG. 8.—The unit cells of the 14 Bravais space lattices. The lattice is continuous in all three dimensions and only the smallest complete units are shown. (1) Triclinic; (2) monoclinic; (3) monoclinic end-centered; (4) orthorhombic; (5) orthorhombic end-centered; (6) orthorhombic body-centered; (7) orthorhombic face-centered; (8) hexagonal, simplest cell is one-third hexagonal parallelepiped; (9) rhombohedral; (10) tetragonal; (11) tetragonal body-centered; (12) isometric; (14) isometric body-centered; (15) isometric face-centered. (From W. L. Bragg, "Atomic Structure of Minerals"; Cornell University Press.)

the crystal can have only one type of lattice. The generalized case is the triclinic lattice, where points occur at corners of a parallelepiped and the interaxial angles and axes are all unequal (Fig. 8-1). The simplest case is the primitive cubic lattice, in which the lattice points occur at the corners of a cube (Fig. 8-12). If the two-dimensional lattice of Fig. 7 were continued in three dimensions, a face-centered cubic lattice would be developed. It should be noted that in the two-dimensional lattice shown in Fig. 7, there are two lattice points per unit cell. This follows from the fact that one lattice point is in the middle of the cell and the four lattice points at the corners are each shared by four cells so that each corner contributes one-quarter point to the unit cell. If an atom was situated at each point of this two-dimensional lattice, there would be two atoms per unit cell; or, if the points were occupied by molecules, there would be two molecules per unit cell. The same idea holds for three dimensions.

The group of symmetry elements characteristic of the *external* symmetry or geometrical form of the crystal are known as the "point group" or "crystal class." There are 32 crystal classes, including a class with no symmetry. Examples of all classes have been found. The symmetry elements that are systematically combined to derive the crystal classes are those given on pages 30 and 31 with the exception of translations, glide planes, and screw axes, for the latter operations are not necessary for the development of symmetry about a *point*.

Geometrically similar faces of a crystal constitute a *form*. For example, the cube is a form with six faces in the hexoctahedral class of the isometric system. The indices of these faces are (100), ($\bar{1}00$), (010), ($0\bar{1}0$), (001), and ($00\bar{1}$). The index of the form is {100}. Each crystal class has seven forms. Unfortunately, crystallographers are not in complete agreement on the terminology used for the names of the forms. It is best to use indices to describe the form, for these cannot be varied and are universally understood.

Each of the 32 classes can be referred to one of six *crystal systems*. These systems are based on the symmetry of the crystal and imaginary reference axes coinciding with certain important directions in the crystal. For example, sodium chloride commonly crystallizes in cubes and belongs to the isometric system. The three axes are taken parallel to the edges with their origin

at a corner of the cube. If the habit of sodium chloride were octahedral, it would still be classified as an isometric crystal because the choice of the axes is based on the type of space lattice. It should be kept in mind that crystals are classified into systems on the basis of their *symmetry* rather than the lengths of the axes and the interaxial angles. For example, a

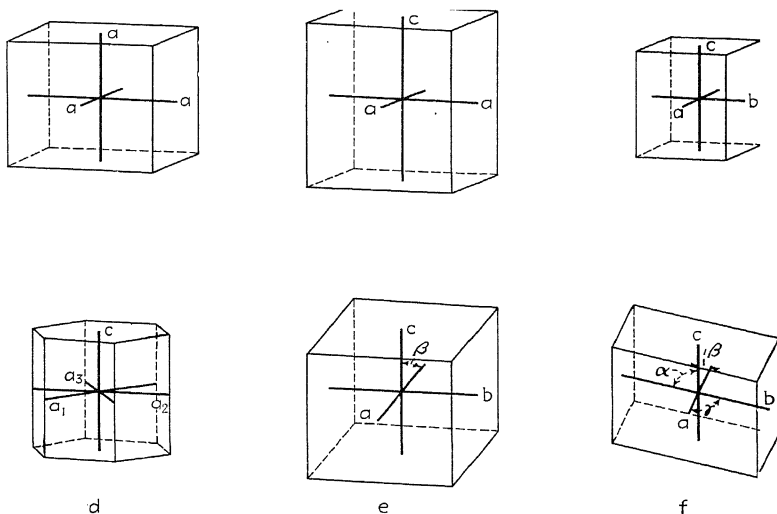


Fig. 9.—The six crystal systems. (a) Isometric, $a = a = a$, all angles 90° ; (b) tetragonal, $a = a \neq c$, all angles 90° ; (c) orthorhombic, $a \neq b \neq c$, all angles 90° ; (d) hexagonal, $a_1 = a_2 = a_3 \neq c$, $c \wedge a = 90^\circ$, $a_1 \wedge a_3 = 60^\circ$; (e) monoclinic, $a \neq b \neq c$, $c \wedge b = 90^\circ$, $c \wedge a = \beta \neq 90^\circ$; (f) triclinic, $a \neq b \neq c$, $a \wedge b = \gamma \neq 90^\circ$, $a \wedge c = \beta \neq 90^\circ$, $b \wedge c = \alpha \neq 90^\circ$.

crystal may sometimes be placed in the orthorhombic system because the axes are orthogonal, whereas X-ray studies reveal a space group consistent with the monoclinic system.

In the following description of the six crystal systems, the letters a , b , and c refer to axes of different length but the a -axes in any one system are of the same length.

Isometric System: Three mutually perpendicular a -axes (Fig. 9a).

Tetragonal System: Two a -axes in a horizontal plane are normal to each other and to the vertical c -axis (Fig. 9b).

Orthorhombic System: Three mutually perpendicular axes a , b , and c (Fig. 9c).

Hexagonal System: Three a -axes making an angle of 120 deg. with one another are in a horizontal plane normal to the vertical c -axis (Fig. 9d). In English textbooks, this system is split into a hexagonal and a rhombohedral system giving seven systems, but this has not been followed by American crystallographers.

Monoclinic System: b and c are in a vertical plane and normal to each other, but a is not perpendicular to this plane (Fig. 9e).

Triclinic System: c is vertical, but the angles between a , b , and c are different and other than 90 deg. (Fig. 9f).

For uniformity in description, crystals are oriented in a special way. The method most often followed is to place the c -axis vertical and parallel to the most highly developed morphological zone; the b -axis is horizontal from right to left; and the a -axis is horizontal from front to back. In the oblique systems, the a -axis slants toward the observer, and the axial angles are indicated in Fig. 9.

Chemically and structurally unlike crystals such as sodium chloride and diamond may have the same crystal system. Nevertheless, the concept of crystallographic axes is as indispensable in the study of crystals as coordinate axes in analytical geometry. They serve as a convenient coordinate system in the study of crystal morphology as well as of crystal structure.

Crystals may occur as intimate intergrowths, parallel growths, and twins. The last are rational, symmetrical intergrowths of two or more individual crystals.

In summary, all crystals have a unique space group that gives the symmetry of the atomic arrangement, a space lattice outlining the general architecture of the crystal, a unit cell containing the smallest unit of the atomic pattern consistent with the symmetry of the crystal and whose dimensions are helpful for classification and identification purposes, a crystal class, and a crystal system. This information can usually be obtained from X-ray diffraction studies. The determination of the arrangement of the atoms in the motif and the actual positions of the atoms is still another story and can be found in the references.

Minerals.—Minerals are homogeneous, inorganic compounds occurring in nature. They are usually solids (water is a notable exception) with characteristic crystallographic, optical, and physical properties. Most minerals are crystalline, and many form well-shaped crystals. Amorphous minerals are uncommon, forming only a small part of the mineral kingdom. Minerals are

rarely pure, and the chemical composition may vary considerably from the theoretical formula. The compositional variation follows definite physicochemical and atomic rules of solid solution. Since the properties of a compound vary with its chemical composition, and minerals are rarely pure, it is extremely important to study these relations as well as the properties of the pure compound. That portion of the discussion will be taken up in the section on crystal chemistry. It should be kept in mind that each mineral species is homogeneous and has a definite crystal structure; consequently, intimate submicroscopic intergrowths of two or more minerals do not constitute a new species.

Although there are about 1,500 mineral species, only a few hundred occur in more than insignificant amounts. The most complete description of the mineral species is in Dana's "System of Mineralogy,"⁽²⁾ which is now being completely revised. Compilations of data on new species are published occasionally in the *American Mineralogist* and the *Mineralogical Magazine* (London). The works of Groth⁽¹²⁾ Doelter,⁽⁷⁾ and Hintze⁽¹³⁾ are also very helpful. Winchell⁽⁴¹⁾ has compiled data for synthetic minerals, and various textbooks on the principles of mineralogy are available.^(44, 15, 88) The tables at the end of Chap. V list the refractory minerals.

Minerals may be formed in a number of ways, such as crystallization from a melt or precipitation from solution, and many minerals can also be made in the laboratory. The latter are sometimes called "artificial," which implies that they are not genuine. This usage is incorrect, since minerals made in the laboratory have the same physical properties and crystal structure as minerals occurring in nature. For example, ruby (a variety of corundum) may be made by melting Al_2O_3 with traces of Cr_2O_3 as a coloring agent. This forms a gem whose physical and chemical properties are identical with that of the natural ruby. On the other hand, a spinel mineral containing vanadium oxide as a coloring agent is often sold as alexandrite. It is an imitation and should be called "artificial alexandrite," since the true alexandrite is BeAl_2O_4 with Cr_2O_3 as a coloring agent and is not a member of the spinel group. Some question may be raised as to the use of the term "synthetic" in the case of the production of such minerals as corundum in the laboratory, because it is not produced by a fusion of aluminum and oxygen

atoms but instead by melting natural Al_2O_3 and hence, in the strictest sense, is not synthesized. Nevertheless, with the exception of the mode of formation and occurrence, there is no essential difference between minerals occurring in nature and those formed in the laboratory or factory. Therefore the term "synthetic" is preferable to "artificial."

Rocks.—Minerals are the integral components of rocks, which therefore can be classified according to the amount of each mineral species present. The most important rock-forming minerals are quartz, feldspar, mica, amphiboles and pyroxenes, feldspathoids, olivine, etc. The assemblage of minerals composing the rock and its texture are characteristic of the rock and its mode of formation. Thus, the mineralogical composition of granites and rhyolites is the same, but their textures are different. The granites contain relatively large crystals because they have crystallized slowly at depth; whereas the rhyolites have cooled relatively rapidly on or near the surface, and consequently their crystals are small. On the other hand, the composition of granite differs greatly from that of gabbro, although the size of the crystals and the textures of the two are similar. Some rocks are composed of only one mineral, notable examples being limestone, composed of calcite, and sandstone, composed of quartz. The texture of such refractory raw materials as magnesite and chromite has an important bearing on their firing characteristics.

2. Crystal Chemistry.—The relationships among chemical composition, physical properties, and crystallographic properties have been long the subject of considerable study and interest. The scope of the work was limited necessarily owing to the fact that the atomic arrangements controlling these relationships could not be determined. During the past twenty-five years of research in the analysis of crystals by X-ray diffraction methods, the crystal structure, *i.e.*, the arrangement and packing of the atoms, of many compounds has been determined.⁽²¹⁾ With the accumulation of structural data, a new field of research or, more correctly, a new viewpoint has emerged which has been called "crystal chemistry." Stillwell⁽⁹⁶⁾ defines it as "the study of (1) the laws governing the arrangement of atoms in solids and (2) the influence of the arrangement and electronic structure of the atoms upon the physical and chemical properties of the solid." }

Crystal chemistry is a rational and fundamental approach to many problems in the fields of ceramics, metallurgy, mineralogy and crystallography, chemistry, and physics, and its great promise in the solution of many diverse problems will be apparent in the following pages. Its very newness (it is not more than fifteen years old) and incompleteness add greatly to its interest. Evans,⁽¹⁰³⁾ Stillwell,⁽⁹⁶⁾ Goldschmidt,⁽²⁸⁾ Hume-Rothery,⁽⁷⁷⁾ and Desch⁽⁵⁷⁾ give interesting accounts of many aspects of crystal chemistry.

For ease in description in the later sections, the capital letters *A*, *B*, *C* are used to denote cations such as Na, Ca, and Ti, and *X*, *Y*, *Z* stand for anions such as Cl, O, and F. Thus a compound written *AX* could represent NaCl or MgO, and *AX₂* could stand for CaF₂, TiO₂, etc. The abbreviation Å. stands for an angstrom unit, which is equal to 10⁻⁸ cm. In the following discussion, the words "atom" and "ion" will be used interchangeably when the usage is not confusing.

Atomic Structure.—All matter consists of very small particles called "atoms." We may think of atoms as being made up of electric charges distributed through a small sphere whose effective radius is of the order of 1 Å. The radius can be measured with great accuracy and is dependent upon the nature of the element, its state of ionization, the manner in which it is bonded to adjacent atoms, and other factors. The mass of any atom is 1.65×10^{-24} g. times its atomic weight, and practically all the mass is confined to the nucleus—an extraordinarily small part of the atom (10⁻¹² cm. in diameter). The nucleus contains the positive charges (protons), neutrons, and other particles. It has a very complex structure whose exact nature has not yet been determined; but it does not enter into our discussion, since it is not concerned in chemical combination.

The extranuclear portion of the atom is made up of electrons, which are negatively charged particles. The mass of an electron is 9.1×10^{-28} g., or 1/1,838 of the mass of the proton. The electric charge of the nucleus determines the number of electrons, and this is given by the atomic number for electrically neutral atoms. Thus, hydrogen with atomic number 1 has one electron; helium with atomic number 2 has two electrons; and so on up to uranium with atomic number 92 and ninety-two electrons. An atom can lose or obtain electrons. If one electron is lost, the

atom is singly positively charged; if two electrons are lost, it becomes a doubly positively charged ion; if the atom gains an extra electron, it becomes a negatively charged ion.

Isotopes are atoms with the same atomic number, different atomic weights, and practically identical chemical properties. When the atomic weight of an element is determined by chemical methods, the mean value of the various isotopes is obtained. Therefore, the atomic weight is not so fundamental as the atomic number, which gives the number of electrons and indicates the chemical properties of the atom.

Modern wave mechanics has shown that we must turn from the simple Bohr model of electrons traveling in definite orbits to a considerably modified and more complex atomic model based on a statistical wave picture. For example, we must now regard the hydrogen atom as a nucleus surrounded by an electron whose probable position in a certain region at a given time is treated by the wave mechanics of Heisenberg and Schrodinger. This complex picture can be simplified by assuming that the magnitude of the force attracting the electron toward the nucleus is dependent only on the distance between them; *i.e.*, it is a central force. In this way, an approximate average position of the electron is obtained that is sufficiently accurate for most purposes.

In the vector model of the atom, each electron is characterized by certain quantum numbers. n is the total quantum number and is an integral number from 1 up. Electrons having $n = 1$ are in the *K* shell; $n = 2$, the *L* shell; $n = 3$, the *M* shell; etc. The lower the total quantum number the greater is the binding energy, and thus electrons in the *K* shell have a higher ionization potential than those in the *L*, *M*, . . . shells. The subsidiary or orbital quantum number l expresses the ellipticity of the orbit and can have any integral value from 0 to $n - 1$; thus, if $n = 3$, $l = 0, 1$, or 2. If $l = 0$, the orbit is spherical; if $l = 1$, the orbit is ellipsoidal; if $l = 2$, the orbit is more ellipsoidal; *i.e.*, the ratio of the major to the minor axes of the ellipsoid becomes larger as l increases. The electrons with $l = 0$ are called *s* electrons; $l = 1$, *p* electrons; $l = 2$, *d* electrons; $l = 3$, *f* electrons. The number of electrons required to complete a shell of quantum number n is $2n^2$, and the number required to complete a subgroup of quantum number l is $2(2l + 1)$.

To illustrate this nomenclature with an actual example, we can use sodium, whose atomic number is 11 and thus has eleven electrons. These electrons are distributed as follows: two s electrons in the spherical K shell, $n = 1$, $l = 0$; eight electrons in the L shell, two of which are s electrons in the spherical subgroup $n = 2$, $l = 0$ and six electrons in the ellipsoidal subgroup $n = 2$, $l = 1$; one s electron (the valence electron) in the M shell $n = 3$, $l = 0$. The notation used to describe this configuration is $(1s)^2(2s)^2(2p)^6(3s)$, where the exponents give the number of electrons in each quantum state, the number in the bracket is the n value, and the letter is the l value. The notation $(2)(8)(1)$ is used to denote the number of electrons in the K , L , M , . . . shells without regard to subgroups; and in this case, there are two electrons in the K shell, eight in the L shell, and the valence electron in the M shell.

s , the spin quantum number, is always equal to $\frac{1}{2}$ and is introduced to represent the angular momentum of the electron about its own axis. (It should not be confused with the s used above to denote the value of an electron $l = 0$.) The quantum number j expresses the total angular momentum of the atom. It is the resultant of the spin and orbital moments.

$$j = l + s \text{ vector}$$

If the atom is placed in a strong magnetic field, two additional quantum numbers are added: m_s , the magnetic spin quantum number, which may be either $+\frac{1}{2}$ or $-\frac{1}{2}$ depending on whether the axis of the spin is parallel or antiparallel to the applied field, and m_l , the magnetic orbital quantum number, which is an integer and may have any value from $-l$ to $+l$. The important principle of Pauli states that *no two electrons in an atom can have an identical set of quantum numbers*. This simply means that no two electrons can be at the same place at the same time. Thus, there can be only two $1s$ electrons, two $2s$ electrons, six $2p$ electrons, etc. Table 5 gives the electronic configurations of the atoms in their normal states.

Figure 10 is a graphical representation of the distribution of the electrons as a function of the radius for the sodium, potassium, and chlorine atoms. Although the picture of electrons moving in regular orbits is no longer tenable, note that the peaks of the curves are rather sharply separated, indicating a large concentra-

tion of electrons in a narrow region. This resembles the familiar idea of electron shells. The following may also be observed from Fig. 10*d*: The *K* and *L* shells of Cl^- are closer to the nucleus than in Na^+ as a result of the higher nuclear charge (and consequently greater attraction) in Cl^- ; the *K* and *L* shells exert a screening effect so that the effective positive charge on the electrons in the *M* shell is reduced, resulting in a much more diffuse distribution

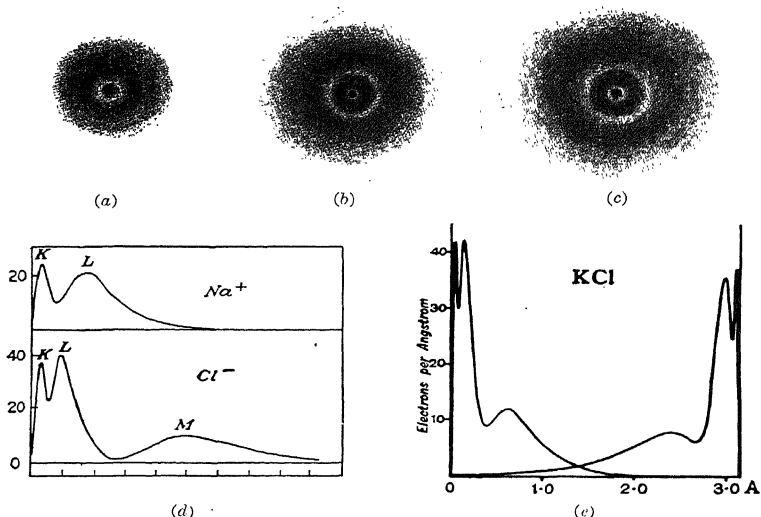


FIG. 10.—Electron concentration as function of atomic radius. (a) Na, (b) K, (c) Cl [Pauling¹⁰⁸]; (d) Na^+ and Cl^- ions [Pauling]; (e) KCl [Bragg,⁵³]; note correspondence of peaks of curves to electron shells. [(a), (b), (c), (d) From Linus Pauling, "Nature of the Chemical Bond"; Cornell University Press, (e) from W. L. Bragg, "The Crystalline State," Vol. I; The Macmillan Company.]

of electrons in the *M* shell. The same is true in the case of KCl (Fig. 10*e*). The drawings in the upper part of Fig. 10 have been taken from Pauling^(108,p.336) and illustrate the same principle, *viz.*, the greater concentration of electrons in certain areas of the atoms.

Atomic Structure and the Periodic Table.—The regular recurrence of elements with similar properties in the Periodic Table results from the electronic structure of the atom. Generally, only the electrons in the outermost shells—the valence electrons

—play a part in chemical reaction, since the inner electrons are too tightly bound to the nucleus. Thus the electronic structure

<div style="display: flex; justify-content: space-between;"> H 1 He 2 </div>																							
<div style="display: flex; justify-content: space-around;"> Li 3 Be 4 B 5 C 6 N 7 O 8 F 9 Ne 10 </div>																							
<div style="display: flex; justify-content: space-around;"> Na 11 Mg 12 Al 13 Si 14 P 15 S 16 Cl 17 Ar 18 </div>																							
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36						
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Ta 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	X 54						
Cs 55	Ba 56	La 57	Ce 58	Pr 59	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Em 86	
<div style="display: flex; justify-content: space-between;"> Fr 87 Ra 88 Ac 89 Th 90 Pa 91 U 92 </div>																							

Class I

Class II Class III

FIG. 11.—Periodic Table arranged to show structural and chemical similarities.

of silver is (2)(8)(18)(18)(1), and the single valence electron in the *O* shell is mainly responsible for its metallic properties. This follows from the fact that the electrons in the *K*, *L*, *M*, and *N*

shells form complete groups and are bound tightly to the nucleus whereas the valence electron is held rather loosely so that electrical conductivity is high and other metallic properties are marked. Figure 11 shows the Periodic Table arranged to emphasize the role of the extranuclear structure. The horizontal rows are the familiar periods, and the lines connect elements of similar properties; the dotted lines are explained below.

If we imagine the consecutive elements being formed by the addition of one electron at a time, we see that the recurrence of similar elements takes place after the formation of complete shells of electrons. The first period contains only two elements, hydrogen and helium, since the K shell ($n = 1$) is complete with two electrons in helium. Lithium is formed by the addition of a third electron which must go into the L shell ($n = 2$), since the K shell can accommodate only two electrons. The second period, lithium-neon, is completed with neon, atomic number 10, which contains two electrons in the K shell and eight in the L shell. Similarly, the third period, sodium-argon, is completed with argon which has two electrons ($n = 1$) in the K shell, eight electrons ($n = 2$) in the L shell, and eight electrons ($n = 3$) in the M shell. The K and L shells containing two and eight electrons, respectively, remain unchanged in elements of higher atomic number. The addition of one and two electrons to the argonlike atom to form potassium and calcium, respectively, is perfectly regular; but when another electron is added to form scandium it enters the inner shell M rather than the outermost shell N . With the further addition of electrons, the M shell expands from nine to sixteen electrons, forming the transition elements scandium-nickel. These elements are important in ceramics as the chief source of color. The remaining elements of the fourth period, copper-krypton, have complete K , L , and M shells; this period is completed with the inert gas krypton whose structure is $(2)(8)(18)(8)$. A similar phenomenon takes place in the fifth period, where the N shell expands from eight to eighteen electrons with the formation of a second group of transition elements, yttrium-palladium. Xenon, $(2)(8)(18)(8)$, completes this period. In the sixth period, another transition group is started with lanthanum. However, with the further addition of electrons, the N shell expands and this gives rise to the rare earth elements cerium-lutecium. The remarkable similarity in

chemical properties of these elements is due to the same electronic structure in the two outer shells; thus in ytterbium, the structure is (2)(8)(18)(31)(9)(2) and in lutecium, (2)(8)(18)(32)(9)(2). The transition group is completed with platinum, and the other elements of this period, gold-radon, are formed by the addition of electrons to the *P* shell. This period is completed with the

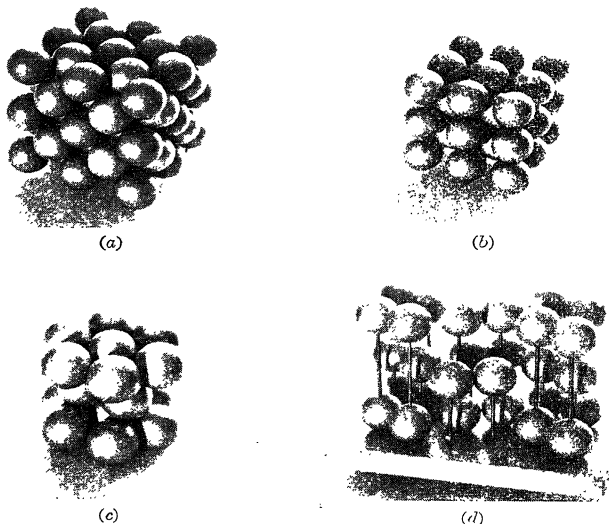


FIG. 12.—(a) Model illustrating the arrangement and packing of atoms in copper, face-centered cubic; each sphere represents an atom of copper. This and other models represent a magnification of about 125,000,000 times. (b) Iron, body-centered cubic. (c) Magnesium, hexagonal close-packed. (d) Chlorine, diatomic molecules; atoms tightly bound (covalent bonds) in pairs forming Cl_2 molecules; but molecules are loosely bound to each other by van der Waals bonds and hence have a low melting point.

last inert gas, radium emanation, whose structure is (2)(8)(18)(32)(18)(8). Table 5 shows the electron configurations of the atoms in their normal states.

An interesting study of the arrangement of the atoms in crystals of the elements has been made by Hume-Rothery. On the basis of their crystal structure, he has divided the elements of the Periodic Table into three groups, shown by the dot-dash lines in Fig. 11. All the elements in Class I have metallic properties,

and all have one of three typical structures: face-centered cubic, hexagonal close-packed, or body-centered cubic. These atomic arrangements are illustrated in Figs. 12*a*, 12*b*, and 12*c*, respectively. The only exceptions are manganese and a form of tungsten, which have complex structures.

The elements of Class III crystallize in such a way that each atom has $8-N$ close neighbors where N (this N is not related to the N of the electron shells, mentioned above) is the number of the column in the Periodic Table to which the element belongs. For example, iodine is in column 7; hence it has $8 - 7 = 1$ close neighbors and accordingly forms diatomic molecules (Fig. 12*d*). In column 6, the atoms in indium, selenium, and tellurium are arranged in spiral chains so that each atom has two closest neighbors; the sulfur structure is similar except the chain forms a closed ring. Arsenic, antimony, and bismuth of column 5 are rhombohedral; the atoms are arranged in double layers; and each atom has three closest neighbors. Carbon [diamond (Fig. 13*b*)], silicon, germanium, and gray tin of column 4 have similar structures in which each atom is surrounded tetrahedrally by four neighbors. The explanation for the structures of the elements in Class III lies in our discussion of the covalent bond: An atom of column N completes its shell by sharing one electron with each of $8-N$ atoms. Since this is characteristic of covalent bonding, these elements are not true metals and do not have metallic properties.

The elements in Class II do not follow any particular rule. Mercury, zinc, and cadmium each have six closest neighbors in accordance with the $8-N$ rule, but these elements have normal metallic properties. Aluminum, indium, thallium, lead, and white tin have structures somewhat similar to normal metals, but the interatomic distances are greater than one would expect, and probably the atoms in crystals of these elements are incompletely ionized.

Tin is unique, since gray tin belongs to Class III and white tin to Class II.

Atomic and Chemical Bonding.—There are three principal types of bonds between atoms in chemical combination: the ionic bond; the covalent, or electron-pair, bond; and the metallic bond. The bonding in each of these extreme types has well-defined properties, but it should be kept in mind that the bonding

in many compounds may be more or less intermediate and the transition gradual. The silicon-oxygen bonds in silica and the silicates are neither pure ionic nor pure covalent but instead are somewhat intermediate and closer to the latter. Evans⁽¹⁰³⁾ has used the term "mesodesmic" to describe these intermediate types of bonds. More than one type of bond can exist in the crystal, *e.g.*, in pyrite, where the iron-sulfur bonds are ionic and the sulfur-sulfur bonds are covalent.

Many of the simplest inorganic salts form *ionic bonds*. In this type of bond, the metallic atoms such as Na or Ag tend to lose their outer electrons and become positive ions, Na^+ , Ag^+ , and nonmetallic atoms such as Cl or I tend to obtain additional electrons and become negative ions, Cl^- , I^- . The electrostatic charges, or coulomb attraction, of the ions hold them together, and repulsion between ions increases abruptly when they are brought within a certain distance of one another. This type of bond is best illustrated by sodium chloride. A neutral sodium atom contains two electrons in the *K* shell, eight in the *L* shell, and one less firmly held electron—the valence electron—in the *M* shell. A neutral chlorine atom has two electrons in the *K* shell, eight in the *L* shell, and seven in the *M* shell. If the sodium atom loses its valence electron, it becomes a positive ion with stable shells; if the chlorine atom obtains this electron, it becomes a negative ion with stable shells. In a sodium chloride crystal, each sodium ion is surrounded by six chlorine ions and each chlorine ion by six sodium ions (Fig. 13c). Therefore, the crystal as a whole is neutral, held together by the coulomb attraction between ions of opposite sign. It should be noted that with the exception of the vapor state, there is no tendency to form molecules, for each ion is surrounded by six others of opposite sign so that no one sodium ion belongs to any particular chlorine ion and vice versa. Radicals such as NO_3^- and SO_4^{2-} may act as single ions and form Na^+NO_3^- or $\text{Ba}^{2+}\text{SO}_4^{2-}$.

In the *covalent bond*, a pair of electrons is shared by two atoms. According to the notation of G. N. Lewis, the electronic structure of a neutral fluorine atom is represented by $\cdot\ddot{\text{F}}\cdot$, whereas two fluorine atoms can combine to give the structure $\cdot\ddot{\text{F}}:\ddot{\text{F}}\cdot$. In these formulas, the symbol of the element represents the nucleus and inner electrons and the dots represent the electrons in the

outer shell. The atoms obtain stable shells in this type of bonding by sharing a pair of electrons. Each electron held in common by the two atoms spends part of the time in one atom, part in the other, and part in the region between the two atoms. Interatomic distances in crystals with ionic bonds are not comparable with those in which the bonding is covalent. The only rule that applies to the sharing of a pair of electrons is that they must have opposite spins in accordance with the Pauli exclusion principle. The principal elements that often form covalent bonds are C, Si; N, P; O, S, Se, Te; H, F, Cl, Br, I. In these groups, four, three, two, or one electrons, respectively, are added to form closed shells.

There is no directional property in the *metallic bonds* in metals and alloys. The crystals are composed of positive ions and loosely held valence electrons. Since there are not enough valence electrons to form stable shells for all the atoms, the electrons are shared by groups of atoms. We may therefore consider a metal as closely packed atoms held together by a neutralizing, mobile electron cloud. The electrical conductivity of metals, a most characteristic property, results from the freedom of motion of the electron cloud. The bonding in metallic crystals is much stronger than the van der Waals' forces but weaker than pure covalent bonding. The strength and non-directional character of the bonds give metals a rather high melting point, great mechanical strength, and plasticity.

The concept of the *van der Waals' forces* originated in his gas law. These bonds are much weaker than the bonds mentioned above and strictly speaking are not true chemical bonds. For example, graphite (Fig. 13a) consists of sheets of carbon atoms in which the *CC* distance between neighbors within a sheet is 1.42Å. and the spacing between the sheets is 3.4Å. The bonding within each sheet is covalent, and the sheets are held together by the weak van der Waals' forces. The lack of strength of the latter is shown by the well-known physical properties of graphite—its softness and its lubricating properties which arise from the ease with which adjacent sheets slide over one another. The bonding within the molecules of many organic crystals is strong, but the molecules are held together by the weak van der Waals' forces. Hence these crystals are easily deformed, very compressible, and have low melting points as a consequence of the

weak intramolecular forces. However, the strength of the van der Waals' forces increases considerably as the size of the molecule increases. In large molecules, *e.g.*, organic plastics, the bond strength between molecules can be considerable even though only van der Waals' forces are acting. These forces are also important in the clay-water system.

The properties associated with the various types of bonds are summarized in Table 6. Refer to Pauling¹⁰⁸ and Richtmyer⁵⁹ for further information.

TABLE 6.—PHYSICAL AND STRUCTURAL PROPERTIES ASSOCIATED WITH THE FOUR PRINCIPAL TYPES OF ATOMIC BONDS
(Evans⁽¹⁰³⁾)

Property	Ionic	Covalent	Metallic	van der Waals
Mechanical	Strong, giving hard crystals	Strong, giving hard crystals	Variable strength. Gliding common	Weak, giving soft crystals
Thermal	Fairly high melting point. Low coefficient of expansion. Ions in melt	High melting point. Low coefficient of expansion. Molecules in melt	Variable melting point. Long liquid interval	Low melting point. Large coefficient of expansion
Electrical	Moderate insulators. Conduction by ion transport in melt. Sometimes soluble in liquids of high dielectric constant	Insulators in solid and melt	Conduction by electron transport	Insulators
Optical and magnetic	Absorption and other properties primarily those of the individual ions, and therefore similar in solution	High refractive index. Absorption profoundly different in solution or gas	Opaque. Properties similar in liquid	Properties those of individual molecules, and therefore similar in solution or gas
Structural	Nondirected, giving structures of high coordination	Spatially directed and numerically limited, giving structures of low coordination and low density	Nondirected, giving structures of very high coordination and high density	Formally analogous to metallic bond

Coordination Number and Radius Ratio.—As an easy introduction to the manner in which atoms pack together and arrange themselves in crystals, let us assume that we have a number of marbles of the same size in a box and that we shake them into closest packing. The marbles will assume an arrangement

familiar to those who have seen cannon balls piled up in the town square. All marbles except those on the surfaces of the pile will be surrounded by 12 other marbles all touching a central marble. The number of nearest neighbors surrounding any one marble is known as the "coordination number"; and, in this case, it is 12. The packing is the same regardless of the absolute radii of the marbles so long as they are all of the same size. This type of atomic packing, illustrated in Fig. 12c (magnesium), is characteristic of metals. At the surfaces of the model, the atoms do not have their full complement of neighbors, but it is easy to picture the environment of an atom in the center of the model.

TABLE 7.—RELATIONS AMONG RADIUS RATIO, COORDINATION NUMBER, AND TYPE OF STRUCTURE FOR IONS A AND X ACTING AS RIGID SPHERES

Radius ratio $R_A:R_X$	Coordi- nation number	Arrangement	Type of structure
	1		Single molecules (argon, neon, etc.), molecular lattices*
Up to 0.15	2	Opposite each other	Double molecules, molecular chains; see chlorine (Fig. 12d)*
0.15-0.22	3	Corners of an equilateral triangle	Boron nitride; see graphite (Fig. 13a),* which has the same structure
0.22-0.41	4	Corners of a tetrahedron	ZnS; see diamond (Fig. 13b),* which has same structure
0.41-0.73	6	Corners of an octahedron	NaCl (Fig. 13c)
0.73 and above	8	Corners of a cube	CsCl (Fig. 13d)
1	12	Closest packing	Cu (Fig. 12a)*

* Not an AX compound.

To make the case more general, let us assume that the marbles are atoms, that they act as rigid spheres, and that we have atoms of different radii, R_A and R_X (the radii of atoms is discussed in the following section). In this case, the packing will be dependent on the *relative* radii of the atoms. For example, sodium chloride (Fig. 13c) is a typical ionic crystal in which each sodium atom ($R_{Na} = 0.98\text{\AA.}$) is surrounded by six chlorine atoms ($R_{Cl} = 1.81\text{\AA.}$) and each chlorine atom by six sodium atoms.

The coordination numbers of both atoms in this structure is 6, and the radius ratio $R_{\text{Na}}:R_{\text{Cl}} = 0.54$. However, in cesium chloride (Fig. 13*d*), the cesium atom ($R_{\text{Cs}} = 1.65\text{\AA.}$) has a coordination number 8 (so has chlorine) because it is considerably larger than the sodium atom. Consequently more chlorine atoms can be packed around it, and the radius ratio in this case

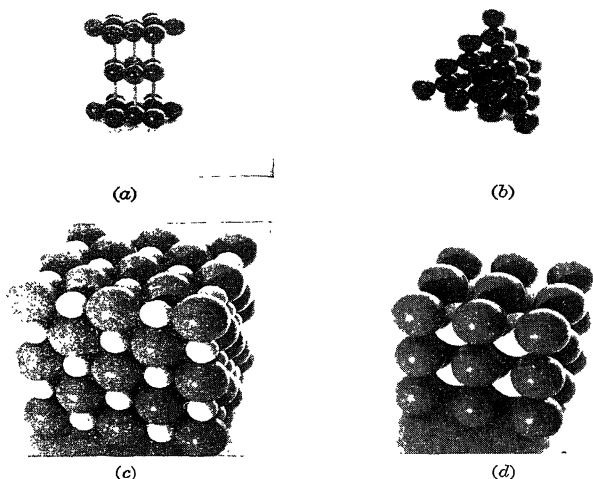


FIG. 13.—(a) Graphite, threefold coordination; (b) diamond, fourfold coordination; (c) sodium chloride, sixfold coordination, large darker spheres Cl^- and smaller white spheres Na^+ ; (d) cesium chloride, eightfold coordination, dark spheres Cl^- , light spheres Cs^+ .

is $R_{\text{Cs}}:R_{\text{Cl}} = 0.91$. It is possible, therefore, to predict the coordination number, radius ratio, and packing on the assumption that the atoms act as rigid spheres. These data for AX compounds are listed in Table 7.

A few examples will aid in the understanding of the principles developed above. The radius ratio of the alkali bromides is

	LiBr	NaBr	KBr	RbBr	CsBr
$R_A:R_X$	0.40	0.50	0.68	0.75	0.84

NaCl structure

CsCl structure

The crystals LiBr-RbBr have the NaCl structure, and CsBr has the CsCl structure. This change in radius ratio, coordination number, and structure is evidently due to the progressive increase in the size of the alkali ions. A similar change in structure could be produced by an increase in the size of the anion as in the series CsF-CsI, in which CsF has the NaCl structure and CsCl, CsBr, and CsI have the CsCl structure. Note that LiBr has the NaCl structure, even though its radius is in the range to have a coordination number 4 according to the data of Table 7. If the radius ratio is on the border line, there is a tendency to form the structure with the larger coordination number because it is the one with the lower potential energy. If this was the only factor, we should then expect RbBr to have the CsCl structure, for its radius is slightly greater than 0.73, the point at which there is a transition from the NaCl to the CsCl structures. One of the additional factors is *polarization*, or "deformability," of the ions. The polarizing power increases with increasing charge and decreasing radius of an ion and is marked in such ions as Ti^{4+} and C^{4+} . Such highly polarizing cations distort the larger, less highly charged anions, a factor that must be taken into consideration, as was pointed out by Goldschmidt. The following series also shows that other factors in addition to radius ratio must be considered: ZrO_2 has eightfold

	SiO_2	TiO_2	ZrO_2	CeO_2	ThO_2
Radius ratio.....	0.30	0.49	0.66	0.78	0.83
Coordination number.....	4	6	8	8	8

coordination in spite of the fact that it is well below the transition value 0.73.

To summarize: (1) The radius ratio $R_A:R_X$ is important in determining the packing arrangements of simple crystals in which the ions behave essentially as rigid spheres; (2) if the radii of the ions in a compound are known, the packing and structure can be predicted; (3) although the concept is also helpful in studying more complex crystals, other factors, particularly polarization, must be considered as well.

Radii of Atoms and Ions.—A discussion and a derivation of the factors involved in determining the sizes of atoms and ions in

crystals are beyond the scope of this book, and the reader may refer to the excellent nonmathematical discussion of this fascinating subject by Stillwell.^(96, Chap. II) Nevertheless, a few of the important features will be indicated. Although atoms are only of the order of an angstrom unit in diameter, their size can be measured with great accuracy by X-ray diffraction methods.

As an example of the methods used to determine the radii of a series of ions, let us consider the well-known case of the alkali halides. The distance, which can be measured accurately by the X-ray methods, between the centers of neighboring ions AX is one-half the unit-cell edge (Fig. 13c). AX for two series of alkali halides are as follows: All have the NaCl structure, and

	LiF	LiCl	LiBr	LiI	
$AX, \text{\AA.}$	2.01	2.57	2.75	3.02	
	LiF	NaF	KF	RbF	CsF
$AX, \text{\AA.}$	2.01	2.31	2.66	2.82	3.01

AX increases with change in anion (LiF-LiI) and cation (LiF-CsF). Since the coordination number remains the same, this progressive increase in AX is evidently due to an increase in the size of the anion in the former case and an increase in the cation size in the latter case. If we know the absolute radius of one of the ions, say fluorine, we can derive the absolute radii of the other ions in the series, provided we assume that they act as rigid spheres in contact with one another. Goldschmidt⁽²⁹⁾ used the absolute radii $F^- = 1.33\text{\AA.}$ and $O^{2-} = 1.32\text{\AA.}$, determined by Wasastjerna by computations based on their molecular refraction. He substituted these values in many series of analogous compounds and derived a set of ionic radii appropriate to sixfold coordination in ionic crystals. For example, in the preceding series, AX in LiF is 2.01. Subtracting 1.33 (F^-) yields 0.68 for the radius of Li^+ . Knowing the radius of Li^+ , we can determine that of Cl^- by subtraction: $LiCl, 2.57 (AX) - 0.68 (Li^+) = 1.89 (Cl^-)$. Similarly the radius of Cs^+ can be determined by subtraction: $CsCl, 3.01 (AX) - 1.33 (F^-) = 1.68 (Cs^+)$. Goldschmidt also derived the ionic radii of the divalent elements from a study of the alkaline earth compounds (see previous table).

and barium oxides; sulfides; selenides; and tellurides) by the substitution method, using $O^{2-} = 1.32\text{\AA}$.

One of the most important results of Goldschmidt's work was the development of the concept of *ionic* and *atomic* radii. He showed that the radius of an element derived experimentally from a particular crystal type can be used as a first approximation in other crystals of the same type but that it cannot be used to compute the radii of elements in another type of crystal. A change in polarization, valence, coordination number, or type of bonding will cause a change in the radius of an element. Thus the radius of the lithium *atom*, Li, in twelvefold coordination in lithium *metal* is 1.50, whereas the radius of the lithium *ion*, Li^+ , determined from an *ionic crystal* is 0.68. The atomic and ionic radii of the elements are listed in Table 8 and shown graphically in Fig. 14; both are taken from Evans.⁽¹⁰³⁾ The atomic values are one-half the distance of closest approach in the structure of the element, and the ionic values are for sixfold coordination.

A number of interesting generalizations have been made by Stillwell⁽⁹⁶⁾ and Evans⁽¹⁰³⁾ from these data. There is a great difference between the radii of an element in the neutral and the ionized states. The positive ion of an element is always smaller and the negative ion is always larger than the neutral atom because the former has lost an electron and the latter has gained one.

	K(atom)	K ⁺ (ion)	Cl(atom)	Cl ⁻ (ion)
Electronic structure.....	(2)(8)(8)(1)	(2)(8)(8)	(2)(8)(7)	(2)(8)(8)
Radius, Å.....	2.31	1.33	0.97	1.81

Highly charged positive ions are small ($Si^{4+} = 0.39$, $C^{4+} < 0.2$), and negative ions are large ($O^{2-} = 1.32$, $Cl^- = 1.81$). The radius decreases with increasing positive charge in a series of positive ions with the same electronic structure. The electronic structures of all the following ions are (2)(8), but the nuclear charge increases, causing a corresponding decrease in ionic radius.

	Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺	S ⁶⁺
Nuclear charge.....	11	12	13	14	16
Radius, Å.....	0.98	0.78	0.57	0.39	0.34

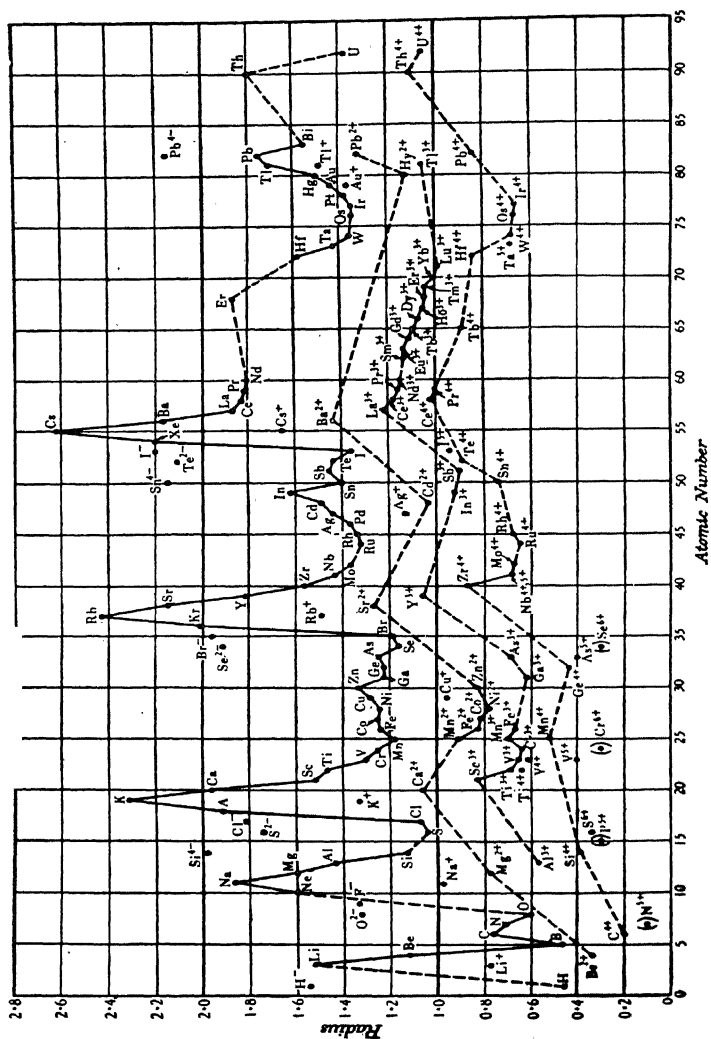


FIG. 14.—Atomic and ionic radii as a function of atomic number. Upper solid lines are atomic radii—one-half the distance of closest approach in structure of the element; lower dotted lines are ionic radii for sixfold coordination. (From R. C. Evans, "An Introduction to Crystal Chemistry," Cambridge University Press.)

TABLE 8

Element	Atomic number	Atomic weight*	Atomic radius†	Ionic radius‡	Ion
Actinium.....	89	227			
Alabamine (?)..	85	221			
Aluminum.....	13	26.97	1.43	0.57	Al ³⁺
Antimony.....	51	121.76	1.45	0.90	Sb ³⁺
Argon.....	18	39.944	1.91		
Arsenic.....	33	79.91	1.25	{ ca. 0.49	As ³⁺
				{ 0.4	As ⁵⁺
Barium.....	56	137.36	2.17	1.43	Ba ²⁺
Beryllium.....	4	9.02	1.12	0.34	Be ²⁺
Bismuth.....	83	209.00	1.55		
Boron.....	5	10.82	0.97		
Bromine.....	35	79.916	1.19	1.96	Br ⁻
Cadmium.....	48	112.41	1.49	1.03	Cd ²⁺
Calcium.....	20	40.08	1.96	1.06	Ca ²⁺
Carbon.....	6	12.01	0.77	0.2	C ⁴⁺
Cerium.....	58	140.13	1.82	1.18	Ce ³⁺
Cesium.....	55	132.91	2.62	1.65	Cs ⁺
Cestium.....	17	35.457	1.07	1.81	Cl ⁻
Chlorine.....	17	35.457	1.07	0.64	Cl ⁻
Chromium.....	24	52.01	1.25	{ 0.3 0.4	Cr ³⁺
				{ 0.6	Cr ⁶⁺
Cobalt.....	27	58.94	1.25	0.82	Co ²⁺
Columbium.....	41	92.91	1.43	0.69	Cb ⁵⁺
				0.69	Cb ⁶⁺
Copper.....	29	63.57	1.28	0.96	Cu ⁺
Dysprosium.....	66	162.46		1.07	Dy ³⁺
Erbium.....	68	167.2	1.86	1.04	Er ³⁺
Europium.....	63	152.0		1.13	Eu ³⁺
Fluorine.....	9	19.000		1.33	F ⁻
Gadolinium.....	64	156.9		1.11	Gd ³⁺
Gallium.....	31	69.72	1.22	0.62	Ga ³⁺
Germanium.....	32	72.60	1.22	0.44	Ge ⁴⁺
Gold.....	79	197.2	1.41	1.37	Au ⁺
Hafnium.....	72	178.6	1.58	0.84	Hf ⁴⁺
Helium.....	2	4.003			
Holmium.....	67	163.5		1.05	Ho ³⁺
Hydrogen.....	1	1.0080	0.16	1.54	H
Illinium (?)..	61	116			
Indium.....	49	114.76	1.62	0.92	In ³⁺
Iodine.....	53	126.92	1.36	2.20	I ⁻
				0.94	I ⁺
Iridium.....	77	193.1	1.35	0.96	Ir ⁴⁺
Iron.....	26	55.84	1.24	{ 0.83	Fe ²⁺
				{ 0.67	Fe ³⁺
Krypton.....	36	83.7	2.01		
Lanthanum.....	57	138.92	1.86	1.22	La ³⁺
Lead.....	82	207.21	1.75	1.32	Pb ²⁺
				0.84	Pb ⁴⁺
				2.15	Pb ⁴⁺
Lithium.....	3	6.940	1.52	0.78	Li ⁺
Lutecium.....	71	174.99		0.99	Lu ³⁺
Magnesium.....	12	24.32	1.60	0.78	Mg ²⁺
Manganese.....	25	54.93	1.18	0.91	Mn ²⁺
				0.70	Mn ³⁺
				0.52	Mn ⁴⁺
Masurium.....	43				
Mercury.....	80	200.61	1.50	1.12	Hg ²⁺
Molybdenum.....	42	95.95	1.36	0.68	Mo ⁶⁺
Neodymium.....	60	144.27	1.80	1.15	Nd ³⁺
Neon.....	10	20.183	1.60		
Nickel.....	28	58.69	1.21	0.78	Ni ²⁺
Nitrogen.....	7	14.008	0.71	0.1 0.2	N ³⁺
Osmium.....	76	190.2	1.35	0.67	Os ⁴⁺
Oxygen.....	8	16.000	0.60	1.32	O ²⁻
Palladium.....	46	106.7	1.37		
Phosphorus.....	15	30.98		0.3 0.4	P ⁺
Platinum.....	78	195.23	1.38		
Polonium.....	84	210			
Potassium.....	19	39.096	2.31	1.33	K ⁺
Praseodymium.....	59	140.92	1.81	1.16	Pr ³⁺
				1.00	Pr ⁴⁺
Protoactinium.....	91	231			

TABLE 8.—(Continued)

Element	Atomic number	Atomic weight*	Atomic radius†	Ionic radius‡	Ion
Radium....	88	226.05			
Radon.....	86	222			
Rhenium....	75	186.31	1.34	0.68	Rh ³⁺
Rhodium....	45	102.91			
Rubidium....	37	85.48	2.43	1.49	Rb ⁺
Ruthenium..	44	101.7	1.33	0.65	Ru ⁴⁺
Samarium...	62	150.43		1.13	Sm ⁴⁺
Scandium....	21	45.10	1.51	0.83	Sc ³⁺
Selenium....	34	78.96	1.16	0.3-0.4	Se ⁶⁺
				1.91	Se ²⁻
Silicon....	14	28.06	1.17	0.39	Si ⁴⁺
				1.98	Si ⁴⁻
Silver.....	47	107.880	1.44	1.13	Ag ⁺
Sodium.....	11	22.997	1.86	0.98	Na ⁺
Strontium...	38	87.63	2.15	1.27	Sr ²⁺
Sulfur.....	16	32.06	1.04	0.34	S ⁶⁺
				1.74	S ²⁻
Tantalum....	73	108.88	1.43	0.68	Ta ⁵⁺
Tellurium...	52	127.61	1.43	0.89	Te ⁴⁺
				2.11	Te ²⁻
Terbium....	65	159.2		1.09	Tb ³⁺
				0.89	Tb ⁴⁺
Thallium....	81	204.39	1.70	1.05	Tl ³⁺
				1.49	Tl ⁺
Thorium....	90	232.12	1.80	1.10	Th ⁴⁺
Thulium....	69	169.4		1.04	Tm ³⁺
Tin.....	50	118.70	1.40	0.74	Sn ⁴⁺
				2.15	Sn ²⁺
Titanium....	22	47.90	1.46	0.69	Ti ³⁺
				0.64	Ti ⁴⁺
Tungsten....	74	183.92	1.36	0.68	W ⁴⁺
Uranium....	92	238.07	1.38	1.05	U ⁴⁺
Vanadium....	23	50.95	1.30	0.65	V ³⁺
				0.61	V ⁴⁺
				0.4	V ⁵⁺
Virginium...	87	224			
Xenon.....	54	131.3			
Ytterbium...	70	173.04	2.20	1.00	Yb ³⁺
Yttrium....	39	88.92	1.81	1.06	Y ³⁺
Zinc.....	30	65.38	1.33	0.83	Zn ²⁺
Zirconium...	40	91.22	1.56	0.87	Zr ⁴⁺

* International atomic weights, 1940, "Handbook of Chemistry and Physics," 24th ed., Chemical Rubber Publishing Co., Cleveland, 1940.

† One-half distance of closest approach in structure of the element; Evans⁽¹⁰³⁾; in angstrom units, 10⁻⁸ cm.

‡ Ionic radii for sixfold coordination; Evans⁽¹⁰³⁾; in angstrom units, 10⁻⁸ cm.

In the case of negative ions, the change is not so pronounced: O²⁻ = 1.32, F⁻ = 1.33.

Isomorphism and Solid Solution.—A knowledge of the chemical composition and particularly the variation in it is extremely important in all types of problems in the solid state of matter. Spectrographically pure compounds are extraordinarily rare, and even chemically pure compounds contain a considerable amount of impurity. To know that a compound is impure is of little interest unless we know how this impurity affects the physical and chemical properties. It is indeed desirable in many problems to vary the chemical composition in order to produce more

desirable physical properties. In this section, we will review compositional variation from the viewpoint of modern crystal structure.

The term "isomorphism" was first applied by Mitscherlich, in 1827, to compounds that had analogous chemical and crystallographic properties and formed solid solutions. More recently, structural crystallographers have applied the term to compounds with analogous crystal structures without regard to their ability to form solid solutions. In this sense, sodium chloride and galena are isomorphous, since they both have the NaCl structure although they do not form mixed crystals. Tutton⁽¹⁴⁾ has suggested the term "isostructural" for such a pair of compounds. In the following discussion, the older usage of the term will be retained.

Variations in composition may be caused by inclusions or admixtures, by regular intergrowths, and by solid solution. The first requires no discussion here, and intergrowths are described later. Neither type is a solid solution even if the intergrowth is submicroscopic, for each compound would give a characteristic X-ray diffraction pattern. There are three principal types of solid solutions: substitutional (or proxy), interstitial, and defect. It is entirely conceivable that inclusions, intergrowths, and all three types of solid solution can cause a variation in composition in the same compound.

Crystal chemistry, particularly the work of V. M. Goldschmidt, has done much to clarify the relations between crystal structure and chemical composition, especially in the formation of solid solutions. Goldschmidt approached the problem from an almost purely geometrical point of view based on numerous lattice parameter measurements. He studied many series of similar chemical compounds and developed empirical rules that have proved extremely helpful in interpreting all types of solid-solution phenomena.

Goldschmidt showed that if the radii of the similar atoms in the two compounds differ from each other by less than approximately 15 per cent of the radius of the smaller atom, and if their polarizability is about the same, they may form wide *substitutional solid solutions* at room temperatures. Other factors being equal, the closer the radii the greater the isomorphism. If the radii are near the limit of tolerance of the structure, only a small amount of isomorphism or none will take place. For example,

fayalite, Fe_2SiO_4 , and forsterite, Mg_2SiO_4 , form a complete series of mixed crystals because they have similar structures and the radii of Mg and Fe^{2+} are similar (0.78 and 0.83 Å., respectively). On the other hand, forsterite and monticellite, CaMgSiO_4 , form only a limited series because Ca (1.06 Å.) is much larger than Mg. Ca_2SiO_4 has a different structure from forsterite owing to the different sizes of the Ca and Mg atoms. Brown and West showed that the symmetry of the forsterite structure could be retained if Ca replaces no more than one-half of the Mg atoms. A greater amount of substitution is not possible because the forsterite structure would be destroyed. In fact, no crystals of this series have been found with $\text{Ca:Mg} > 1:1$.

It does not matter if the atoms that substitute for one another have a different valence as long as the radius is in the favorable range and the polarizability is similar. Thus Na^+ (0.98 Å.) can replace Ca^{2+} (1.06 Å.), but Na^+ and K^+ (1.33 Å.), which are more closely related chemically, do not ordinarily form isomorphous series owing to their great difference in ionic radii. However, the net valence of the crystal must remain balanced; therefore the unbalance in valence caused by the substitution of a divalent cation for a univalent cation must be compensated by a concomitant substitution of, say, a divalent cation for a trivalent cation or by the addition of a univalent anion. This geometrical limitation explains why certain compounds can form more or less complete solid solutions whereas some pairs of close chemical similarity form only narrow or no solid solutions.

At higher temperatures, a greater difference may be tolerated by the structure owing to the expansion of the lattice by the thermal energy. For example, Cr_2O_3 and Al_2O_3 form a complete series of mixed crystals at high temperatures.^(39,36) At low temperatures, however, two partial series of mixed crystals are formed. One series, rich in Cr_2O_3 , is colored green, and the other, rich in Al_2O_3 , is colored red.^(18,46) Similarly, although NaCl and KCl form a complete series of mixed crystals at high temperatures, they are immiscible at room temperature. A further example is found in the feldspars. At high temperatures, the potash and the plagioclase feldspars are miscible; but at room temperatures, they are immiscible. The potassium often reported in small amounts in the plagioclases is probably due to small amounts of impurities (such as potash feldspar or mica). When a mixed crystal of a

miscible series cools and is unable to retain those atoms whose radii exceed the tolerance limit at lower temperatures, exsolution or polymorphism may take place.

In order that two compounds may form a complete series of substitutional solid solutions with each other, their chemical formulas must be analogous and they must have similar crystal structures in addition to the geometrical requirements imposed by the radii of the atoms. For example, only about 18 per cent iron can replace zinc in sphalerite, ZnS , and there is no complete series between sphalerite and troilite, FeS , owing to the fact that they have totally different crystal structures although ferrous iron and zinc have the same radii. Moreover, some structures are more amenable to substitution than others. Thus the spinels form many isomorphous series, but the quartz structure has little tolerance and almost invariably occurs as pure SiO_2 .

If the atoms are very small, they may fit into the interstices of even close-packed structures and form solid solutions without the necessity of substitution. Hydrogen, carbon, boron, and nitrogen, all tiny atoms, often enter into *interstitial solid solution*. Both substitutional and interstitial solid solutions may exist in the same crystal, as in manganese steel, in which manganese atoms substitute for iron and the carbon atoms are interstitial. If the compound has an open-packed structure, or large openings, interstitial solid solution may take place with large atoms. The alkali atoms in glass, for example, occupy the open parts of the silica framework. This mechanism is also important in base exchange and polymorphism.

In solid solutions with *defect lattices*, some of the atoms are missing, leaving vacancies in the structure. A good example is pyrrhotite, which has more sulfur than is indicated by the simple formula FeS . Sulfur is too large to be interstitial in the pyrrhotite structure, and the variation may be due to the fact that sulfur replaces some of the iron atoms or that the sulfur remains constant and some of the iron atoms are missing. Hägg and Sucksdorff⁽⁴⁹⁾ showed by unit-cell and density measurements that the latter is the case. Crystals with defect lattices have interesting electrical properties which are important in certain specialized fields of ceramics.

If the cations of one compound occupy the positions of the anions in the other compound, as in AX_2 and A_2X , they will not

form solid solutions even though they have similar structures and other factors are favorable. Such a pair of compounds is antiisomorphous.

If two compounds enter into solid solution with each other, their properties (specific gravity, refractive index, conductivity, lattice parameter, etc.) are related serially to the chemical composition. The relationships are not so apparent in interstitial and omission solid solution as in substitutional solid solution. The dependence of properties on chemical composition

A X A X A X A X	B X B X B X B X
X A X A X A X A	X B X B X B X B
A X A X A X A X	B X B X B X B X
X A X A X A X A	X B X B X B X B
A X A X A X A X	B X B X B X B X
X A X A X A X A	X B X B X B X B
AX	BX
Compound	Compound
(a)	(b)
A X A X B X A X	A X B X A X B X
X B X A X B X B	X B X A X B X A
B X A X A X A X	A X B X A X B X
X A X B X A X B	X B X A X B X A
B X A X A X B X	A X B X A X B X
X B X B X B X A	X B X A X B X A
(AB)X	ABX
Solid solution	Superstructure
(c)	(d)

FIG. 15.—Structure of hypothetical compounds. (a) AX compound; (b) BX compound with same structure as AX; (c) solid solution of 50 per cent AX and 50 per cent BX forming (AB)X; X retains same positions as in (a) and (b) but A and B have random arrangement; (d) superstructure ABX; A and B atoms occupy special positions increasing the identity period (indicated by arrows).

is due to the fact that the atoms playing the same role in each of the compounds occupy similar positions in the solid-solution structure and that hence the crystal structure of any intermediate member is similar to that of the end members. The atoms that substitute for one another are randomly arranged in the positions that they may occupy in the solid-solution structure (this is called a "disordered structure"), for otherwise a superstructure (called an "ordered structure," see page 69) would form. This is shown diagrammatically in Fig. 15 for two hypothetical

compounds forming a complete series. The structure of compound AX is shown to be the same as that of BX , and the A and B atoms and the X atoms occupy similar positions in each compound. This structural arrangement is retained in any intermediate member, as shown in Fig. 15c for a member consisting of 50 atomic per cent of each of the end members ($A_{0.5}, B_{0.5}$) X . Again the X atoms occupy the same positions as in the end members, but the A and B atoms are randomly arranged in the special positions that they occupied in the end members. An indefinite number of other cations, C, D , etc., and anions, Y, Z , etc., could replace A and B or X provided they had favorable sizes and the cation-anion ratio was not changed.

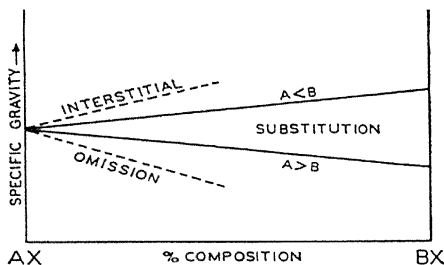


Fig. 16.—Specific gravity as a function of composition in various types of solid solutions. (Hypothetical.)

The repeat period, as determined by X-ray diffraction analysis, is an average over many millions of unit cells, and the parameters of any intermediate member, $(A_x, B_{1-x})X$, are between those of AX and BX . Vegard showed that the unit-cell size of any intermediate member of a primary solid-solution series is related to the size of the unit cell of the end members by a straight line. Precision measurements show that the relationship departs from linearity; more often a contraction and sometimes an expansion are noted. Figure 16 (assume that lattice parameter instead of specific gravity is plotted against composition) gives the linear relationship for a pair of hypothetical compounds AX and BX that form a complete solid-solution series. If A is smaller than B , any intermediate member will have a greater lattice parameter than A ; if A is greater than B , any intermediate member will have a smaller lattice parameter than A . This

important rule, which was first developed with ionic salts and later extended to metals, has been used recently in metallurgical work to study phase-rule diagrams. Although it is very helpful in studying simple systems, it may not be of great use in complex compounds. For example, if a number of atoms, some of which are larger and some smaller than the atoms that they are replacing, are entering in substitutional solid solution, it is entirely conceivable that no significant change in the lattice parameter may be apparent, since the average size of the replacing atoms may be about the same as the atom or atoms that they are replacing. Of course, if the two atoms are of the same size, there will be no change in lattice parameter. In the cases of interstitial and defect solid solutions, the lattice parameter changes will not be so great as in the case of substitutional solid solution.

In favorable cases, careful specific-gravity measurements may be used to supplement X-ray data in distinguishing among the various types of solid solutions. Figure 16 shows specific gravity as a function of the composition in two hypothetical compounds A_2X and BX forming a complete series. In the case of substitutional solid solution, if the A atoms are heavier than B atoms, the other members will have a lower specific gravity; if the A atoms are lighter than B , the other members of the series will have a greater specific gravity. In interstitial solid solution, the line will be much steeper because atoms are being added and none removed. In defect solid solution, since atoms are omitted, intermediate members will have a lower specific gravity.

The correct formula showing the isomorphism can be obtained directly from the chemical analysis if the structure of the compound or similar compounds is known. At least some knowledge of the structure is necessary in order to know which atoms are equivalent. Magnesiochromite, a mineral of the spinel group, may serve as an example. The formula is determined from the atomic contents of the unit cell as indicated at the end of the analysis shown in the table on page 65.

Spinel has a close-packed structure (Fig. 17b); and, with the possible exception of silicon, none of the atoms present are small enough to form interstitial solid solution. In order to simplify the discussion, we shall not consider the possibility of defect solid solution or variate atomic equipoints⁽⁴²⁾ and shall confine our attention to substitutional solid solution. The radii of

silica, lime, and water are not in the correct range to substitute for the other atoms; and, from a knowledge of the associated minerals, they are probably present as an admixed impurity, most likely serpentine. Although titania has the correct radius to substitute for other elements, studies of other spinels show that it probably does not and hence the chemical analysis has

	I	II	III	IV		V	VI	VII	
MgO	14.83	14.88	40.32	0.369	Mg	0.369	0.369	5.65	} 8.10
FeO	11.35	11.39	71.84	0.158	Fe ²⁺	0.158	0.158	2.42	
MnO	0.14	0.14	70.93	0.002	Mn	0.002	0.002	0.03	
NiO					Ni				
Cr ₂ O ₃	55.51	55.71	152.02	0.366	Cr	0.732	1.098	11.21	} 16.18
Al ₂ O ₃	14.03	14.08	101.91	0.138	Al	0.276	0.414	4.23	
Fe ₂ O ₃	3.79	3.80	159.68	0.021	Fe ³⁺	0.048	0.072	0.74	
SiO ₂	0.24				O			32.4	
TiO ₂	0.17								} 32.4
CaO	0.11								
H ₂ O ⁺	0.07								
H ₂ O ⁻	0.02								
	100.26	100.00					2.113		

I. Chemical analysis, weight per cent; analysis by Dr. R. B. Ellestad given by A. L. Parsons, *Magnesiochromite from Carbon Pit Coleraine Township, Quebec: Univ. Toronto Studies, Geol. Ser.*, No. 42, pp. 75-78, 1939.

II. Column I recalculated to 100 per cent after deducting SiO₂, TiO₂, CaO, H₂O.

III. Molecular weight.

IV. Molecular quotient = II/III.

V. Atomic quotient of cation = IV × number of cations.

VI. Atomic quotient of oxygen = IV × number of oxygen atoms.

VII. Atomic contents of unit cell = atomic quotient × molecular weight M of unit cell $ZM = (GV \times 10^{-24}) / (1.663 \times 10^{-24})$; Z is the number of formula weights in a unit cell; it is an integer and is eight in spinel; 1.663×10^{-24} is the absolute weight of the hydrogen atom; G is measured specific gravity; V is volume of unit cell; $ZM = 1,531$ taking G as 4.5; and V is 562 from the measured $a_0 = 8.247$.

been recalculated to 100 per cent (column II) after subtracting these elements. Of the remaining atoms, the ionic radius of the smallest is aluminum (0.57Å.) and a 15 per cent tolerance would bring this value up to 0.66. The only atoms with radii in the favorable range to substitute for aluminum are Cr³⁺ (0.64Å.) and Fe³⁺ (0.67Å.). According to evidence obtained from X-ray studies, these substitutions do take place even though Fe³⁺ slightly exceeds the favorable range. Another series of atoms, Mg (0.78Å.), Fe²⁺ (0.83Å.), Mn (0.91Å.), and Ni (0.78Å.), have radii favorable for isomorphism, and any one can take the place

of a magnesium atom in the structure. Oxygen (1.32\AA .) occupies still other positions. The sum of the atomic contents of atom

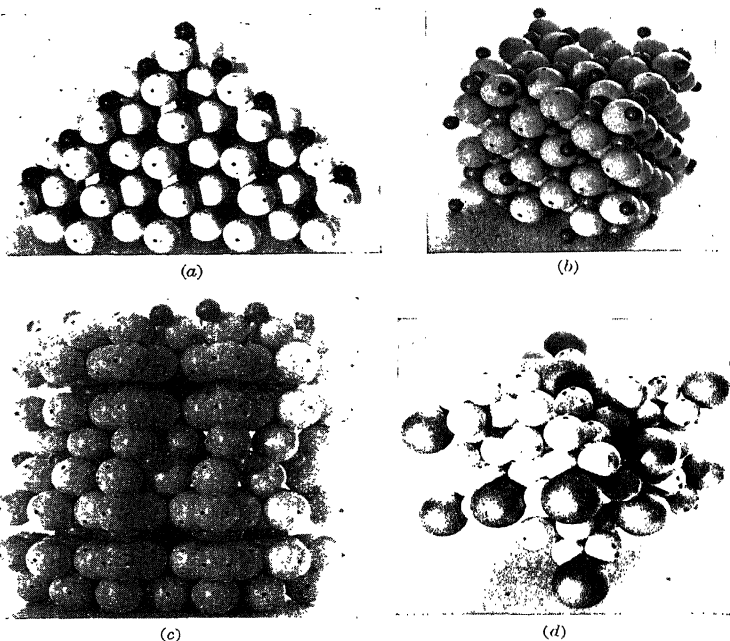
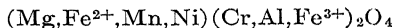


FIG. 17:—(a) Hematite, Fe_2O_3 ; small black spheres represent iron atoms and large white spheres oxygen atoms. α -corundum has same structure. (b) Spinel, MgAl_2O_4 ; smallest spheres represent aluminum, larger dark spheres are magnesium, and large white spheres are oxygen. (c) Muscovite; perpendicular to c -axis, showing double silicate sheet in middle and large potassium atoms (only partially visible) holding one double sheet to next. Perfect cleavage is parallel to double sheets. (d) Sanidine; large dark spheres are potassium in close-packed silica framework, white spheres are oxygen. Silicon nestles in tetrahedron of four oxygen atoms and is not visible.

that substitute for one another is shown in the brackets; the chemical formula may now be written



and there are eight formula weights per unit cell. The reasons why the sums are not integral numbers (*e.g.*, 8.10 instead of 8.00 for the divalent cations) may be the result of errors in the chem-

ical analysis, in specific gravity, or in the measurement of the unit cell.

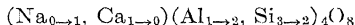
Much of the literature of ceramics and mineralogy gives the formulas of minerals in the molecular form, *i.e.*, in terms of the number of molecules of the constituent oxides. This can be illustrated by the well-known example of the plagioclase feldspars. The molecular formula of albite is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, and of anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. However, there is no sound physical basis for writing the formulas in this manner. It is preferable to write $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$, respectively, for there are no molecules of CaO , Al_2O_3 , or any other oxide in the plagioclases. Although the great majority of organic crystals are made up of molecules, the crystal structure of most minerals is definitely not molecular. The nonexistence of molecules in minerals is vividly shown by the crystal-structure models in this chapter.

The model of the crystal structure of sanidine (Fig. 17*d*) is similar to that of the plagioclase feldspars. The large, dark spheres represent potassium atoms, which are replaced by calcium and sodium atoms in the plagioclases. The smaller white spheres are oxygens, and silicon and aluminum are not apparent in this picture because they nestle in a tetrahedron of four oxygens. The structure is a three-dimensional silica framework in which each oxygen is shared by two adjacent tetrahedrons with aluminum proxying for silicon in the tetrahedrons and the alkali atoms occupying the large open spaces in this network. An alkali atom is not associated with a special oxygen atom, nor are the aluminum or silicon atoms bonded to particular oxygens. Instead, each calcium is surrounded by *six* oxygens; each aluminum and each silicon is surrounded by *four* oxygens; and this network is *continuous* in all three dimensions.

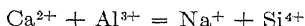
The halite structure is another illustration showing the absence of molecules in minerals. In this case, each ion is surrounded by six others of the opposite sign and the alternation of Na^+ and Cl^- ions continues throughout the crystal (Fig. 13*c*). Therefore, since no sodium ion belongs to any particular chlorine ion (and vice versa), we cannot speak of NaCl molecules in the solid state. We can now see that the molecular formulas do not give a picture of the structure of the crystal. Atomic formulas give a clearer picture and are particularly helpful in discussing such phenomena

as isomorphism and the relation of physical properties to chemical composition.

The formula of albite should be written $\text{NaAlSi}_3\text{O}_8$, and of anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$. The general formula of any plagioclase is then



It was pointed out above that atoms could substitute for one another in solid solution provided their radii were not very different. In this series, Ca^{2+} and Na^+ can proxy for each other, and so can Al^{3+} and Si^{4+} , since the radii of each pair are in the range favorable for substitution. For each Ca^{2+} ion introduced in place of Na^+ , an extra positive charge is introduced. This is compensated by a similar substitution of Al^{3+} for Si^{4+} in an oxygen tetrahedron, and the *double* substitution

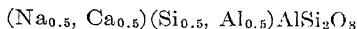


causes no net change in valence charges.

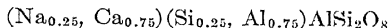
The general formula of the plagioclases can now be written in the more useful form



where x represents the composition of any member of the series; i.e., $x = 1$ for albite; $x = 0$ for anorthite. Thus the formula of an intermediate member of equal proportions of the end member is



and a member consisting of 75 atomic per cent of the anorthite-rich member



Berman further points out the dangers in the practice of writing the formulas of mixed crystals as if they consisted of two components. According to this practice, a mixed crystal of the forsterite-monticellite series would be represented by m per cent $\text{Mg}_2\text{SiO}_4 + n$ per cent Ca_2SiO_4 . Crystal-structure studies show that neither of these molecules is found in the structure. Ca_2SiO_4 is not even a member of the series. Instead the formula should be written $(\text{Mg}, \text{Ca})_2\text{SiO}_4$ with the Mg:Ca ratio shown. "The

mistake of using probable components to express intermediate composition has led to the common practice of proposing so-called 'end-members' which have often no existence and thereby confuse the study of the constitution of the silicates.^{77(81,p.350)} The ratio Mg:Ca, which need not be an integral number, fully expresses the position of the solid-solution member in the series.

If the atoms of a completely miscible pair of compounds, AX , BX , assume special positions forming, say, vertical rows of AX , XB , BX , XA , AX , . . . , a superstructure is formed. As a result of this special arrangement, shown in Fig. 15*d*, the identity period is increased and symmetry lowered. Such an atomic arrangement has a lower energy and hence greater stability than the disordered solid-solution arrangement, and also its properties are different. They are often found in alloys and sulfides. The tendency for the formation of superstructures may be increased by slow cooling and annealing so that the equivalent atoms can move to the special positions. There seems to be some question as to whether they should be regarded as distinct compounds or special forms of solid solutions. Other factors being equal, there is more chance for superstructures to form if the diameters of the equivalent atoms are neither too similar nor too unequal. In other words, if the size factor is too favorable, the atoms may interchange so freely that the random solid solution is almost as stable as the superstructure; and, if the atoms differ too greatly, there may be more of a tendency to form regular compounds. For a further discussion, see the interesting work of Hume-Rothery^(77,p.77) which also includes a number of important references.

Polymorphism.—The term "polymorphism" refers to the existence of a single chemical substance in more than one solid crystalline form. In the well-known case of iron, the α -form is body-centered cubic and is stable up to 909°C. It inverts to the face-centered cubic γ -form when this temperature is exceeded and the latter inverts to the δ -form (body-centered cubic) at 1403°C. which is stable to the melting point. When the temperature is reduced, the high-temperature forms revert to the forms stable over the lower temperature ranges. Each form may have its distinct set of physical properties. The classic example of the transition of white tin (tetragonal) to gray powder (cubic, diamond-type structure) at 18°C., often called the "tin pest,"

is an extreme case. There are many well-known cases of polymorphism such as SiO_2 , ZrO_2 , CaCO_3 , ZnS , and S , and it is probable that many more substances have polymorphic modifications than is suspected at present. A knowledge of the causes and mechanisms operative in the formation of polymorphous forms is most important in the study of matter in the solid state, and an excellent critical review of the literature has been published by Buerger and Bloom.⁽⁸⁵⁾

If two phases have closely similar structures, as shown in Figs. 18a and 18b, so that only a slight reorientation of the atoms

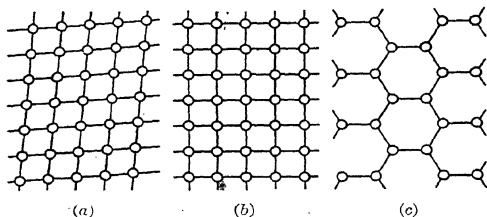


FIG. 18.—Hypothetical two-dimensional lattice. $a \rightarrow b$, or $b \rightarrow a$, prompt inversion; $a \rightarrow c$, $b \rightarrow c$, or $b \rightarrow c$, or $c \rightarrow a$, sluggish inversion. (W. A. Weyl, *Bull. Am. Ceram. Soc.*)

and bonding angles in one phase will produce the other phase, the inversion will be rapid and probably reversible. On the other hand, if the two phases have considerably different structures (compare Figs. 18c with 18a or 18b), the conversion of one form to the other will be sluggish and probably irreversible because the phase change necessitates a drastic rearrangement of the atoms and the breaking of many bonds. This is also shown by the crystal-structure models of silica minerals (Fig. 19). The atomic arrangements of the high- and low-temperature forms of quartz or cristobalite are similar, but the cristobalite, tridymite, and quartz structures differ considerably from one another. The high-temperature forms of silica are open packed with large holes, whereas both high and low quartz are close packed. The coordination number of silicon in all cases is 4; *i.e.*, the silica tetrahedrons are present in all the forms of silica, and each tetrahedron shares all four oxygen atoms with neighboring tetrahedrons, but the bond angles between the tetrahedrons in the different structures are different. Hence the high-low or low-

high transformations of each mineral are rapid and reversible, but the transformation from quartz to tridymite, for example, is sluggish and irreversible owing to the fact that their structures

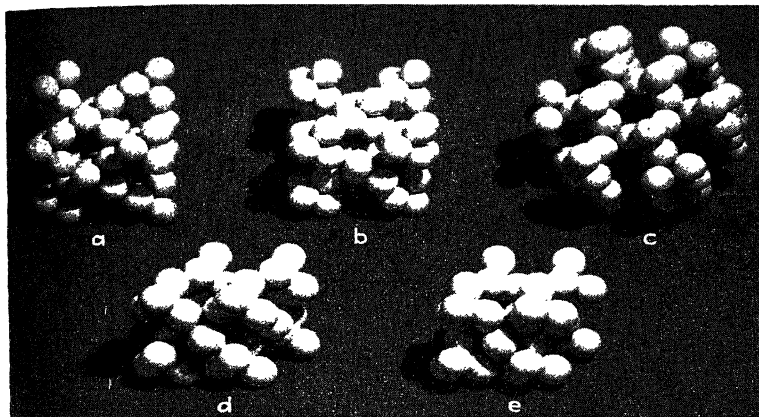


FIG. 19.—Models showing atomic arrangements in polymorphic modifications of SiO_2 . (a) High-cristobalite; (b) low-cristobalite; (c) high-tridymite; (d) high-quartz; (e) low-quartz. Models not in parallel crystallographic orientation; silicon atoms nestle in oxygen tetrahedrons and are not visible; high-temperature forms are more open-packed than low-temperature forms.

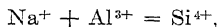
are so different. This matter is discussed further in the section on silicates.

TABLE 9.—CHANGE OF STRUCTURE TYPE WITH INCREASING IONIC RADIUS IN THE CARBONATES

Formula	Radius, \AA^{2+}	Mineral	Structure type
MgCO_3	0.78	Magnesite	Calcite
FeCO_3	0.83	Siderite	Calcite
ZnCO_3	0.83	Smithsonite	Calcite
MnCO_3	0.91	Rhodochrosite	Calcite
CaCO_3	1.06	Calcite	Calcite
CaCO_3	1.06	Aragonite	Aragonite
SrCO_3	1.27	Strontianite	Aragonite
BaCO_3	1.43	Witherite	Aragonite
PbCO_3	1.32	Cerussite	Aragonite

Goldschmidt approached the problem of polymorphism from the geometrical viewpoint of coordination number and ionic size.

doubled, owing, presumably, to the alternation of silicon and aluminum atoms in the oxygen tetrahedra (AlO_4 and SiO_4 tetrahedra). Furthermore, the nepheline-carnegieite transformation corresponds to the tridymite-cristobalite transformation. Both carnegieite and nepheline can be considered to be impure cristobalite and tridymite structures, respectively, because the atomic arrangements are the same except that sodium and aluminum atoms are introduced. Al^{3+} substitutes for Si^{4+} in the oxygen tetrahedra, and half the voids in the silica framework are filled with Na^+ so that the double substitution,



leaves the valence unchanged. Thus, we can think of carnegieite and nepheline as being high-temperature silica framework structures with interstitial and substitutional solid solution.

The low-temperature form of silica, quartz, is closely packed and provides no large interstices for alkali ions to compensate for the aluminum-silicon substitutions. Hence, it almost always occurs as pure SiO_2 , and impurities found in analyses are due to admixture rather than solid solution. If the melt from which SiO_2 crystallizes is impure, it follows that quartz will not form and, instead, one of the high-temperature modifications, tridymite or cristobalite, will result. Only a few chemical analyses are available, but they indicate that both tridymite and cristobalite are impure forms of SiO_2 . Hence, the inversion of tridymite or cristobalite to quartz may be prevented by impurities as well as their differences in structure and bond angles. The inversion cannot be effected until the impurities are removed. Many examples could be cited as evidence of this picture of the problem. For example, Peyronel⁽⁷⁸⁾ made cristobalite by heating a silica gel with a melt of NaPO_3 at temperatures below 750°C . Cristobalite has been found in opal,⁽⁴⁵⁾ which is formed in nature at low temperatures. The decomposition of sillimanite, Al_2SiO_5 , into mullite, $\text{Al}_3\text{Si}_2\text{O}_{13}$, and cristobalite, SiO_2 , rather than into quartz is to be expected because of the presence of aluminum atoms. Taylor and Lin⁽¹²⁴⁾ found that the inversion temperature of quartz to cristobalite or tridymite varied with the type of compound used to promote the reaction because the different catalysts are taken into solid solution to a greater or lesser degree. The low-high cristobalite inversion varied from

220 to 253°C. depending on the type of catalyst. It is now apparent that the so-called "anomalous" existence of phases far below their range of thermodynamic stability is not at all anomalous, since the structure of the precipitated phase bears no necessary relation to thermodynamic stability. Crystal structure and precise chemical composition must be considered.

Hardness.—In general, the hardness decreases with increasing distance between the atoms if the charge of the ions is constant. The higher the charge the greater is the hardness. This is shown by the data for some simple compounds in Table 10. The distance between the centers of cation and anion, AX , is given in angstroms, and the hardness is the relative scratch hardness (Mohs' scale). The decrease in hardness with increasing interatomic distance takes place if the latter is caused by an increase in the cation size, BeO-BaO , or anion size, CaO-CaTe . Note that BeO has a hardness of 9, and it is interesting that Eisenlöffel⁽¹²⁶⁾ found beryllium glasses to have an unusual hardness. The last group of compounds, NaF-TiCl , shows an increase of hardness with increasing charge of the ions. The greater the charge the more tightly bound are the ions, and hence these compounds have a greater hardness. The interatomic distance and charge should not be considered as playing separate roles, since the latter is at least partially responsible in determining the value of the former.

The hardness may vary with crystallographic direction due to crystal structure, although this variation is smaller than that caused by the factors mentioned above. One of the most extraordinary examples of the variation of hardness with crystallographic direction is kyanite, Al_2SiO_6 . Parallel to the c -axis, the hardness is $4\frac{1}{2}$; and perpendicular to c , it is 7. Such large variations are rare.

Compounds with layer structures are usually softer than related compounds not having a layer structure (*e.g.*, graphite and diamond). The following have also been noted^(44,p.215): (1) Compounds of heavy metals (silver, copper, mercury, lead) are usually less than 3; (2) sulfides, arsenides, and oxides of iron, nickel, and cobalt are relatively hard (pyrite = 6, hematite = 6); (3) sulfides, carbonates, and phosphates are relatively soft, except as noted in (2); (4) hydrous compounds are usually softer than equivalent anhydrous compounds (zeolites are soft,

and feldspars are relatively hard; gypsum = 1.5 – 2, anhydrite = 3 – 3.5); (5) conspicuously hard minerals are chiefly oxides, carbides, and borides.

TABLE 10.—RELATIONSHIPS AMONG INTERIONIC DISTANCES, HARDNESS, AND MELTING POINT

	BeO	MgO	CaO	SrO	BaO	
<i>AX</i>	1.65	2.10	2.40	2.57	2.77	
Hardness (Mohs).....	9.0	6.5	4.5	3.5	3.3	
Melting point, °C.....	2510	2800	2570	2430	1923	
	CaO	CaS	CaSe	CaTe		
<i>AX</i>	2.40	2.84	2.96	3.17		
Hardness (Mohs).....	4.5	4.0	3.2	2.9		
	NaF	NaCl	NaBr	NaI		
<i>AX</i>	2.31	2.79	2.94	3.18		
Melting point, °C.....	988	801	740	660		
Thermal expansion, ($\alpha \cdot 10^6$)....	39	40	43	48		
	NaF	CaF ₂	CaO	ThO ₂	ScN	TiC
<i>AX</i>	2.31	2.36	2.40	2.42	2.23	2.23
Valence ratio.....	1:1	2:1	2:2	4:2	3:3	4:4
Hardness (Mohs).....	3.2	4.0	4.5	6.5	7.8	8.9
Melting point, °C.....	992	1330	2570	3030		3140

Cleavage.—Cleavage takes place along directions of minimum atomic bonding strength. Wooster⁽⁹⁸⁾ has compiled some interesting empirical rules which are summarized below relating crystal structure and cleavage. If the spacings between a number of atomic planes of a crystal are the same or nearly the same, all may be cleavage planes; but if there are relatively large differences in the interplanar spacing, cleavage will take place parallel to the planes of greatest spacing. The exceptions to this rule are that cleavage never breaks up radicals in ionic crystals or molecular complexes in covalent crystals. In addition, the cleavage is always between sheets or chains of atoms in structures where these motifs are well defined, since the bonding

within these groups of atoms is stronger than the forces holding one sheet or chain to the next.

The cleavage of ionic crystals may be summarized as follows: (1) All cubic crystals of composition AX (alkali halides, galena, etc.) have cleavages parallel to $\{100\}$. (2) Cleavages may separate but never break up radicals; *e.g.*, the cleavage planes in barite, $BaSO_4$, pass between SO_4 radicals. Similarly, the cleavage of crystals containing SiO_4 and CO_3 radicals, etc., leaves these groups intact. (3) In crystals without radicals, cleavage occurs between planes of anions; *e.g.*, fluorite cleavage $\{111\}$ takes place between planes of fluorine ions; planes of large cations may be exposed by the cleavage if planes of anions are not present.

Covalent crystals also show definite types of cleavages: (1) The greatest spacing in diamond (Fig. 13b) is $\{111\}$, coinciding with its perfect cleavage. $\{111\}$ in sphalerite, ZnS , corresponds to planes with zinc atoms on one side and sulfur atoms on the other. However, the cleavage is $\{110\}$, which are planes with equal numbers of zinc and sulfur atoms on either side. (2) Cleavage may separate but not break up molecules. For example, stibnite is made up of $(Sb_4O_6)_n$ molecules forming chains parallel to the c -axis. Although the covalent bonding within the molecules is strong, the lateral forces between the chains are weak and thus stibnite crystals have excellent cleavage parallel to the c -axis.

A somewhat analogous type of cleavage takes place in silicates with chain structures. The ionic forces between the cations and the silica framework are not so strong as the covalent bonding within the framework. Therefore, we should expect that the best cleavages are in directions that do not cut across the silica framework but instead pass through the relatively weak lateral bonds. In the case of asbestos, a double-chain amphibole, the mineral can be readily split into flexible fibers parallel to the silica chains by an applied force so small that it leaves the chains intact. On this basis, Warren showed the reason for the difference in cleavage angle of the pyroxenes and amphiboles, which is such an important diagnostic feature of these minerals.⁽³⁰⁾ In both cases, cleavage is parallel to the silica chains and takes place between the calcium-oxygen or magnesium-oxygen bonds which hold the chains together. An end view of the chains, indicated by blocks in Fig. 21, shows that the double chains of

the amphiboles are longer in the b direction than the single chains of the pyroxenes; consequently, the intersections of traces of cleavages in the latter form almost square blocks (93 deg.), whereas the angle between the cleavage planes of the amphiboles is more acute (56 deg.).

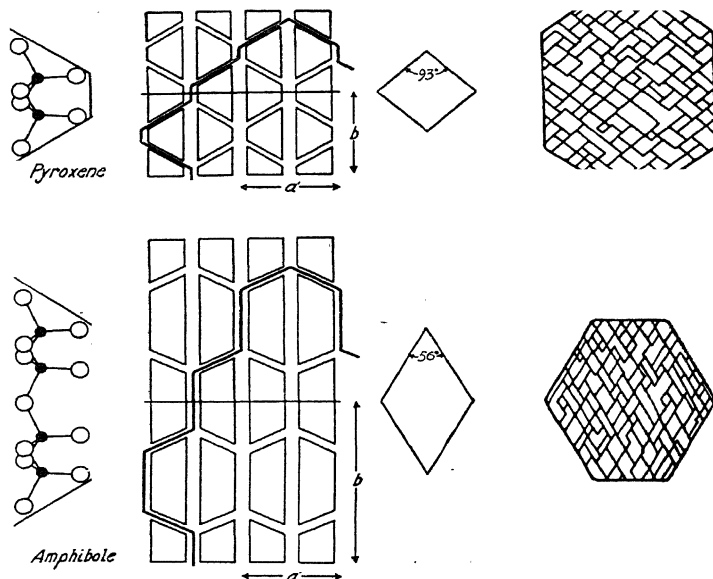


FIG. 21.—Dependence of cleavage angle on silica chains in pyroxenes and amphiboles. (From W. L. Bragg, "Atomic Structure of Minerals"; Cornell University Press.)

In layer structures, without exception, the cleavage takes place parallel to the layers because the bonding within the sheet is stronger than the forces holding the sheets together. In graphite (Fig. 13a), the forces within each sheet are homopolar but only weak van der Waals' forces hold one sheet to the next. Consequently, the mineral has excellent basal cleavage; and in addition, since one sheet can readily slide over its neighbor, graphite is a good lubricant. Molybdenite has a similar cleavage. The silicates with sheet structures exhibit a somewhat similar type of cleavage. Muscovite is made up of double silica sheets

(Fig. 17c). The homopolar silicon-oxygen bonding within each single sheet is very strong; and as two single sheets are bound together by strong aluminum-oxygen bonds, each double sheet acts as a unit. The double sheets are bound to each other by large potassium atoms which are shared by twelve oxygens, six from each double sheet. The mica cleavage, which is the most perfect of all minerals, takes place between the relatively weak potassium-oxygen bonds and forms thin elastic sheets. However, in contrast to graphite, in which the sheets are bound only by very weak van der Waals' forces, the double sheets of muscovite are held together comparatively firmly by the potassium-oxygen ionic bonds; therefore they cannot readily glide over one another. The silica sheets in kaolinite, talc, pyrophyllite, etc., are bonded only by weak van der Waals' forces as in graphite; consequently, these minerals are very soft and plastic.

Minerals with a three-dimensional silica framework, such as quartz, have no cleavage because the bonds are very strong in all directions. However, many minerals whose structures are based on this type of network, such as the feldspars and zeolites, have one or more good cleavages. Their structures are very complex and cannot be discussed here because a detailed structural analysis is necessary for an adequate explanation. W. H. Taylor⁽⁵¹⁾ has noted that the {001} and {010} cleavages of orthoclase are parallel to the silica network where it forms "rings" around the open spaces housing the large cations.

The importance of a knowledge of the cleavage of minerals is closely related to the plasticity of fine particles with water. Platelike particles, such as kaolinite, have a high plasticity, as discussed in Chap. VII.

Deformation of Solids.—When stress is applied to a solid, the first strain produced is elastic; and as soon as the force producing the strain is removed, the distortion that has taken place is also removed. If a greater force is applied, the elastic limit may be passed and either the solid will fracture without deformation (*i.e.*, it is brittle) or it will deform plastically (*i.e.*, it will not return to its original shape when the force is removed). Most substances are deformed by a combination of the two, and even most of the plastic substances may ultimately yield by fracture. The type of deformation that takes place depends on a number of variables: magnitude and direction of the applied force, rate of

Thermal Expansion.—It is not possible to predict the thermal expansion of compounds from our present knowledge. The coefficient of thermal expansion of the elements is roughly periodic, but there are so many irregularities that we must look

TABLE 11.—ANISOTROPY OF THERMAL CONDUCTIVITY IN RELATION
TO CRYSTAL STRUCTURE
(After Wooster⁽⁸⁰⁾)

	k_{\perp}/k_{\parallel}	Observed	Calculated	Calculated
Group 1:*				
Rutile.....		0.62	0.83	
Corundum..		0.85	0.74	
Anhydrite..		0.94†	0.97	
		0.89‡	1.00	
Zircon.....		0.81	0.84	
Group 2:§	k_{\perp}/k_{\parallel}		k_1/k_3	k_2/k_3
Graphite..	4.0			
Gypsum...			0.64	0.42
Mica.....			5.8	6.3
Group 3:				
Cinnabar..		0.72		
Anatase...		0.80		
Quartz¶...		0.58		
Stibnite...			0.47	0.29
Tremolite.			0.36	0.57

k_{\perp}/k_{\parallel} = ratio of conductivities perpendicular and parallel to the optic axis; k_2 = conductivity parallel to [010] in orthorhombic and monoclinic crystals; k_1 and k_3 = principal conductivities parallel to [100] and [001] in orthorhombic crystals, and they lie in plane of (010) in monoclinic crystals.

* Bonds have approximately same strength throughout crystal.

† k_1/k_2 .

‡ k_2/k_1 .

§ Crystals with layer structures.

|| Crystals with chain structures.

¶ Classification of quartz with chain-structure crystals is questionable.

Additional data on crystals are given in Chap. XVII.

for other factors besides atomic number for an explanation. In a study of nonmetallic crystals, Megaw⁽⁹⁵⁾ developed an empirical approximation that holds fairly well for many simple ionic crystals. She found that

$$\alpha = \frac{c}{Q^2}$$

where α = the coefficient of thermal expansion ($\times 10^6$)

c = a constant

q = the electrostatic share

The latter is equal to the charge on an ion divided by its coordination number or number of surrounding ions of opposite sign and is obtained from a knowledge of the crystal structure of the compound. In other words, the expansion coefficient of a crystal is inversely proportional to the square of its electrostatic share. A number of α -values of compounds are shown in Table 71, Chap. XVI.

Melting Point.—The melting point of a compound also affords a rough measure of the strength of its interatomic bonding. The data of Table 10 show that the melting point, as in the case of hardness, decreases with increasing interatomic distance, NaF-NaI, and is higher for compounds with higher ionic charges, NaF-TiC. Stillwell⁽⁹⁶⁾ also notes the following: The melting point increases with decreasing anion size; varies irregularly with the size of the cation until corrected for the radius ratio effect; is lower for layer lattices than for ionic crystals and lowest for molecular crystals; and decreases as the number of anions per cation increases.

Related topics such as lattice energy and heat of formation are discussed by Stillwell⁽⁹⁶⁾ and Seitz.⁽¹²¹⁾ A further discussion of this subject is given in Chap. XII.

3. The Silicate Minerals.—Because of the great importance of the silicates in the refractories industry, considerable space will be devoted to this particular group of minerals. Much of the early mineralogical work on the silicates is summarized by Doelter⁽⁹⁾ and Clarke⁽⁸⁾ and will not be reviewed here. Up to the past ten or fifteen years, the silicates were considered to be salts of various hypothetical silicic acids. Since these acids were not synthesized or identified in solutions of these minerals, they could not serve as a rational basis for an adequate general theory. The constitution and crystal chemistry of the silicates remained a perplexing problem, but many of its major aspects have been recently clarified by X-ray diffraction analysis initiated particularly by W. L. Bragg, Warren, and their coworkers. Although the determination of the atomic arrangements of the silicates is extremely difficult and only about 15 per cent of the known silicates have been completely analyzed, we now have a general

classification and a clearer picture because most of the principal structural types are known. The chemical composition and many of the properties of silicates are now seen in relation to the atomic arrangements; consequently a fundamental and more rational interpretation is now possible.

One of the most important contributions of crystal chemistry has been in the interpretation of isomorphism and the complex compositional variation in the silicates, and we shall see the importance of these concepts in the following pages. A complete and detailed structural classification is still not possible because of the comparatively small amount of structural data available. However, Berman,⁽⁸¹⁾ Strunz,⁽⁹¹⁾ Swartz,⁽⁹²⁾ and others have made excellent studies, based on the pioneering work of Machatschki⁽²⁵⁾ and W. L. Bragg.⁽³¹⁾ The proposed classification by Berman is probably correct in its major aspects and includes a detailed discussion of the compositional variation and the structural and physical relationships of the various species. The most detailed account of the structures of the silicates is given by W. L. Bragg, in "Atomic Structure of Minerals."⁽⁸²⁾

X-ray diffraction studies show that in silicates and silica, each silicon atom occurs in the center of a tetrahedron formed by four oxygen atoms. This SiO_4 tetrahedron (Fig. 23a) is the fundamental unit and forms the important motif of the framework of the silicates. Tetrahedrons may be linked by sharing an oxygen atom, or they may exist as distinct units. The rule governing the linking of tetrahedrons is simple: They can share only corners but never edges or faces owing to the high repulsion between the tetravalent silicon atoms. The structural classification is based on the geometry of the linking of the tetrahedrons. For example, if no corners are shared, the tetrahedrons exist as separate units, a formation that characterizes the orthosilicates. If one corner is shared, one oxygen atom is common to two tetrahedrons and this characterizes the pyrosilicates; if two corners of a tetrahedron are shared, two oxygen atoms are common to two tetrahedrons (metasilicates). In the disilicates, three corners are shared, and all four corners are shared in the silica-type minerals. The silicon-oxygen ratio of the chemical formula, discussed below, varies with the number of corners shared. Table 12 summarizes the pertinent data on the structural classification of the silicates.

One of the most important results of X-ray analysis of the silicates was the discovery that aluminum can play a dual role. The aluminum-oxygen radius ratio is 0.43, which is close to 0.414, the critical value for the transition from sixfold to fourfold coordination. Hence aluminum atoms may occur in either type of coordination, and often both types occur in the same

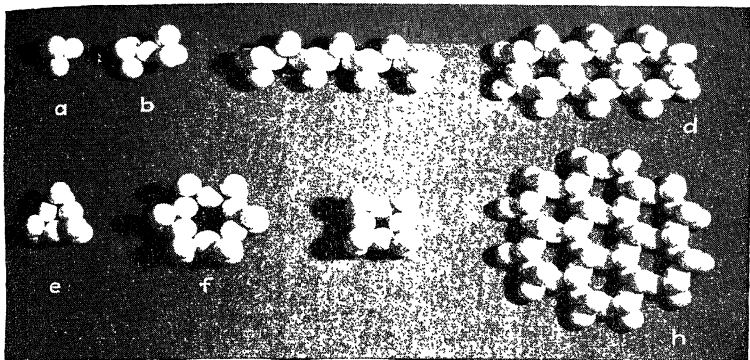


FIG. 23.—The fundamental silica motifs of the silicates. (a) Independent single tetrahedron (SiO_4 , orthosilicates). (b) Independent pair of tetrahedrons sharing one oxygen atom (Si_2O_7 , pyrosilicates). (c) Continuous single-chain linkage, each tetrahedron shares two oxygen atoms (SiO_3 , metasilicates, pyroxenes). (d) Continuous double-chain linkage, each tetrahedron shares alternately two and three oxygen atoms (Si_4O_{11} , metasilicates, amphiboles). (e) Closed independent ring of three tetrahedrons each sharing two oxygen atoms (Si_3O_9 , metasilicates, benitoite). (f) Closed independent ring of six tetrahedrons each sharing two oxygen atoms (Si_6O_{18} , metasilicates, beryl). (g) Closed independent ring of four tetrahedrons each sharing two oxygen atoms (Si_4O_{12} , apophyllite). (h) Continuous planar silica sheet each tetrahedron sharing three oxygen atoms (Si_4O_{10} , disilicates, mica).

mineral, *e.g.*, in the micas. When aluminum is in fourfold coordination, it takes the place of silicon to form AlO_4 tetrahedrons and an indefinite amount of substitution may occur. The substitution may be random, one group of oxygens apparently not being favored more than another. In these cases, an appropriate amount of aluminum is added to the silicon-oxygen ratio. When aluminum is in sixfold coordination, it plays the same role as other cations such as ferric iron and magnesium. One atom can substitute for another atom provided they are of approximately the same size, and often a number of atoms take part in the substitution as explained in the section on isomor-

phism. The valencies of individual ions need not be the same, but the *aggregate valence must remain unchanged*, because the total number of oxygen atoms remains fixed since they are the ions that determine the general nature of the network. Thus a substitution of Al^{3+} for Si^{4+} produces a net valency deficiency of -1 , which must be compensated by a corresponding substitution

TABLE 12

Type	Silica motif	Si:O ratio of smallest unit	Valence charge of silica unit	Example	Formula
Orthosilicates	Independent tetrahedrons sharing no oxygens. Do not form glasses readily	1:4	-4	Forsterite	Mg_2SiO_4
Pyrosilicates	Independent pairs of tetrahedrons sharing one oxygen	2:7	-6	Åkermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$
Metasilicates: Chains	Continuous single chains of tetrahedrons sharing two oxygens	1:3	-2	Diopside (pyroxenes)	$\text{CaMg}(\text{SiO}_3)_2$
	Continuous double chains of tetrahedrons sharing alternately two and three oxygens	4:11	-6	Tremolite (amphiboles)	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Rings	Closed independent rings of tetrahedrons each sharing two oxygens	3:9	-6	Benitoite	$\text{BaTiSi}_3\text{O}_9$
		6:18	-12	Beryl	$\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$
Disilicates	Continuous sheets of tetrahedrons each sharing three oxygens; forms planar hexagonal network	4:10	-4	Muscovite	$\text{KAl}_2(\text{Si,Al})\text{O}_{10}(\text{OH})_2$
Silica	Three-dimensional 1:2 continuous network of tetrahedrons each sharing all four oxygens. Readily form glasses	1:2	0	Quartz	SiO_2
		1:2	0	Orthoclase	KAlSi_3O_8

of Ca^{2+} for Na^+ or Fe^{3+} for Fe^{2+} , etc. In addition to the cations, the anions $(\text{OH})^-$ and F^- may statistically replace each other. These possible atomic substitutions give rise to a great amount of compositional variation; and in some cases (*e.g.*, hornblende), the chemical formula cannot be written with integral numbers for the individual elements. In the formulas listed on the

following pages, all atoms in the same bracket can substitute for one another even though they may have different valencies; the only condition that must be satisfied is that the positive and negative valencies throughout the formula are balanced.

The net valence of the silica framework is negative; the metallic elements occupy interstitial positions and neutralize the negative charge. These cations are also surrounded by a characteristic number of oxygen atoms, although their coordination number may vary in different compounds. Thus, sodium and calcium are surrounded by six or eight oxygen atoms; titanium, by six; zirconium, by eight; ferrous iron, by four, six, or eight; etc.

The bonding within the silica framework is much stronger than the bonding between the metal cations and the framework, and consequently the cleavage planes of the silicates are parallel to silica chains or sheets. The bonding within the SiO_4 tetrahedron is somewhat intermediate between ionic and covalent and probably closer to the latter. For a more extended discussion, see Slater⁽¹¹¹⁾ who treats the bonding as covalent and Pauling⁽¹⁰⁸⁾ who treats it as ionic. The term "mesodesmic" has been applied by Evans⁽¹⁰³⁾ to this intermediate type of bonding. There is little doubt, however, that the bonding between the cations such as Mg^{2+} , Fe^{2+} , etc., and the silica framework is ionic.

We will now take up the various types of silicates and see how the chemical composition and physical properties of the silicates are mainly dependent upon the silica framework which forms the largest bulk of the crystal.

Orthosilicates.—The orthosilicates, which are of particular interest in refractories because of their high fusion point, are made up of isolated silica tetrahedrons bonded by the metallic atoms. Since no corners are shared with other tetrahedrons, the silicon-oxygen ratio is 1:4. The charge of a single tetrahedron is -4 , ($4\text{O}^{2-} + 1\text{Si}^{4+} = -4$), which is balanced by the metallic elements. Thus the general formula of the orthosilicates is A_2SiO_4 , in which A represents the cations such as Mg^{2+} , Ca^{2+} , etc., that balance the negative charges of the silica framework. The orthosilicates form a chemically diverse group of minerals; sodium and potassium are scarce; and the rare earth and other rare elements are often present. Important orthosilicates include forsterite, Mg_2SiO_4 ; olivine, $(\text{Mg},\text{Fe})_2\text{SiO}_4$; willemite, Zn_2SiO_4 ; Ca_2SiO_4 ; zircon, ZrSiO_4 ; topaz, $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$; and the

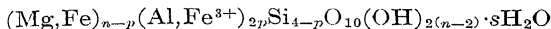
inasmuch as adjacent sheets are displaced parallel to the base, the crystals have a symmetry lower than hexagonal and are often monoclinic. In their recent excellent study, Hendricks and Jefferson⁽¹⁰⁴⁾ showed that the stacking of the sheets may be irregular, and considerable crystallographic complications are introduced into this relatively simple presentation of the matter. The sheets form a dominant and practically invariable part of the structure; and in almost all of these minerals, $a = 5.1$ to 5.3\AA . and $b = 9.0$ to 9.3\AA . Two sheets may be strongly bonded to each other and form a pair of sheets, which is a characteristic unit of the mica minerals, or the structure may consist of single sheets as in the kaolin minerals. The variations of the physical properties of the disilicates are due to the various ways in which the sheets are stacked on one another and especially to the strength of the bonding between them. Most of the disilicates have a medium hardness, but those containing a large amount of water are soft.

Muscovite (Fig. 17c) is a type example of a paired-sheet disilicate. The double sheet consists of pairs of single sheets with their apexes pointing toward each other. The pairs are tightly bonded to each other by such atoms as aluminum, magnesium, or iron in sixfold coordination. The double sheets are bonded comparatively loosely to each other by alkali and alkaline earth atoms in the micas, by water layers in the vermiculites, or by magnesium-aluminum hydroxide layers in the chlorites, or there are no linking atoms between the sheets as in talc and pyrophyllite. The perfection of the cleavage, hardness, and the plasticity of these minerals is dependent upon the bonding strength between each of the double sheets that act as units.

The composition of these minerals is quite complex. The general formula of the mica group is $A_{0-1}(B,C)_{2-3}D_4O_{10}(O,OH,F)_2$ where A is predominantly K; $B = \text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Li}$; C is mainly Al and Fe^{3+} ; and D represents Si and Al with the Si:Al varying from 5:3 to 7:1. Some of the aluminum is in tetrahedral coordination, and the composition of the unit of each sheet is $\text{AlSi}_3\text{O}_{10}$.

In talc, $\text{Mg}_3\text{Si}_2\text{O}_{10}(\text{OH})_2$, and pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, none of the aluminum is in tetrahedral coordination. Here each double sheet is neutral, and there are no atoms linking the double sheets, which consequently are very soft and have an easy cleav-

age. The general formula of the chlorite family is



where $n = 6$ or less

$p = 2$ or less

Chlorite flakes are not elastic, contain a comparatively small amount of alkalis, have a larger proportion of (OH) than mica, and are much softer than the micas. Two types of water give rise to the characteristic dehydration curves of the chlorites. The loosely held H_2O is driven off at low temperatures, but, since the (OH) is more firmly held in the structure, the mineral must be heated to a comparatively high temperature to drive it off.

The clay minerals are discussed fully in Chap. V, as they are very important to the ceramist.

Silica-type Minerals.—In these minerals, all four oxygens of the tetrahedron are shared to form a continuous three-dimensional silica network (Fig. 19). Since each silicon atom is surrounded by four oxygens and each oxygen by two silicons, the composition is SiO_2 . Quartz (Figs. 19*d* and 19*e*), type member of this group, is discussed with the other silica minerals. It is close packed and has homopolar bonding in all directions which forms a very strong and rigid crystal somewhat like diamond but not so hard. It is logical to classify quartz and the other silica minerals with the silicates rather than with the oxides. The structure, occurrence, and physical properties support this change in classification.

Most of the minerals of this type have large openings in an otherwise closely packed silica framework. The alkali elements, calcium, and the more unusual components such as Cl, S, CO_3 , and SO_4 are housed in these openings. As a result of the large holes in the network, these minerals have a rather low mean refractive index and their density is often between 2 and 3. They have a tendency to form equidimensional crystals. Aluminum takes the place of silicon in some of the tetrahedrons, and the valence balance is retained by the entrance of alkali and alkaline earth elements into the structure. Examples of this group include orthoclase, KAlSi_3O_8 (see Fig. 17*d*); albite, $\text{NaAlSi}_3\text{O}_8$; labradorite, $(\text{Na,Ca})\text{Al}(\text{Al,Si})\text{Si}_2\text{O}_8$; anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$; the nepheline and the sodalite groups; and the zeolite family.

Minerals with three-dimensional silica networks readily form glasses by the usual treatment because it is difficult for the

atoms to rearrange themselves into their former rigid framework on cooling. The tendency to form glasses is greatest in the silicates with a Si:O ratio of 1:2, becomes progressively less as the ratio is increased, and is least in the orthosilicates.

Subsilicates.—If the silicon-oxygen ratio falls below 1:4, some of the oxygens are not in tetrahedra and these minerals merge into nonsilicates where the silica tetrahedron is no longer the dominant motif. Berman calls these “subsilicates”; and with the exception of dumortierite, $\text{AlB}_3\text{Si}_3\text{O}_{19}(\text{OH})$, all are rare and not well understood.

4. Crystal Growth and Related Phenomena.—The growth of crystals occurs in the firing of all refractories; and as the physical properties of the finished product are often influenced by the number, size, and shape of these crystals, it will be seen how important is a knowledge of this subject.

It is well known that growth from a melt or solution does not take place simultaneously in all parts of the container. The studies of DeCoppet,⁽⁴⁾ Tamman,⁽¹⁷⁾ and Othmer⁽¹⁰⁾ have shown that the development of spontaneous nuclei is purely a chance phenomenon and that the region of metastability is a function of the time that one is willing to wait for the formation of crystals as well as of the size of the sample used, the shape of the container, and other factors. Crystallization can also be initiated by a seed crystal from which growth then proceeds. For example, Norton found, in his study of crystalline glazes, that crystals could be produced at any desired location by seeding and that their size could be controlled by the growing time and their shape by the growing temperature.⁽⁸⁷⁾ Tamman⁽¹⁷⁾ has treated this matter in detail and has shown that if the temperature of nuclei formation and crystal growth coincided, spontaneous crystallization took place but that if they occurred at different temperatures, the number and size of crystals could be accurately controlled. Advantage is taken of this fact in making opal glasses.

In crystals, each unit cell is surrounded by other unit cells of exactly the same atomic contents, and arrangements and hence the interior of the crystal must be electrically neutral. In solid solutions, the contents of one unit cell may differ from its neighbor but the average contents of the unit cells throughout the interior of the crystal are the same. In the case of zoned crystals, the

average contents of the unit cells are the same only within each zone. However, there is an open force field at the surface of the crystal. This surface force field varies with the atomic arrangements, interatomic distances and radius ratio, polarizability, and bonding between the atoms. The surface forces control many crystallographic phenomena such as crystal growth, adsorption, oriented overgrowths, and intergrowths. We shall now briefly discuss each of these phenomena in relation to the surface forces of the crystal.

Crystal Growth.—It was once believed that the rate of growth of a crystal face was dependent upon the reticular density of that face. The planes of more closely packed atoms were believed to grow slower (and hence become the dominant faces of the crystal, as explained below) than planes in which the atomic packing was less dense. If the growth rate was dependent entirely upon the reticular density, we should expect faces on the opposite ends of a polar axis to have the same growth rate, since their reticular densities are the same; however, they usually grow at different rates. Furthermore, the reticular densities of the same forms of adjacent members of an isomorphous series must be similar, and hence, according to this theory, one would expect the growth rate of that form to be about the same in all members of the series. This, too, is not supported by experimental evidence. It has been observed that certain forms may have large growth velocities in one member and slow growth velocities in the next member of the series. Crystal growth is a more complex phenomenon than the reticular density theory indicates; and although an all-inclusive quantitative picture has not yet been developed, we can present facts that are in closer agreement with observable phenomena.

If a small cubical crystal of sodium chloride is placed in a supersaturated water solution of sodium chloride, the crystal will begin to grow. This means that at the surface of the crystal, there are unsaturated affinities capable of attracting additional ions and hence enabling continuation of crystal growth. In general, the growth velocity of the various crystallographic forms of the crystals is different. In other words, the growth velocity of a crystal is vectorial.

If we place a sphere of sodium chloride instead of a cube in this supersaturated solution and permit growth for a compara-

tively short time, the sphere will develop a large variety of forms with spherical areas in between. If the sphere is permitted to continue growth, a number of the forms originally observed will become smaller or disappear and the remaining forms will have grown larger. The longer growth continues the greater is the tendency for the cube $\{100\}$ to become the dominant form of the crystal because it has the slowest growth velocity. If we represent this variation in growth velocity with crystallographic

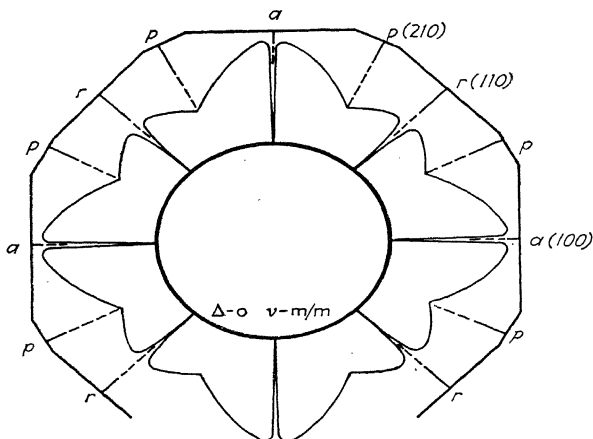


FIG. 24.—Growth-velocity vector diagram of NaCl. Vectors are smallest normal to slowest growing (most dominant faces) of the crystal. (Rinne ⁽¹⁶⁾.)

direction by vectors drawn from the center of the crystal, the bounding surface formed by the vectors has sharp minima corresponding to the very slow-growing forms. This is shown in Fig. 24 for $\{100\}$, $\{110\}$, and $\{210\}$ of sodium chloride. In this case, the growth velocities are $\{210\} > \{110\} > \{100\}$, so the dominant forms of the crystal are $\{100\} > \{110\} > \{210\}$.

Figure 25, from Desch, further illustrates how the slow-growing forms become the dominant forms of the crystal. The shaded areas represent the original hypothetical crystal. Faces ab and de grow with the least velocity and become faces on the completed crystal. cd has the maximum and bc an intermediate growth velocity. Neither of these appears on the completed crystal, but mn , which was not present on the original crystal,

appears soon after growth begins and becomes larger. Face mn would finally give way to the more slowly growing forms ab and de , which is indicated by the slope of the edges between the neighboring faces. Hence the faster growing forms may appear on very small crystals; but, as the crystals increase in size, they are overgrown by the slower growing forms, the latter becoming the dominant forms of the larger crystals.

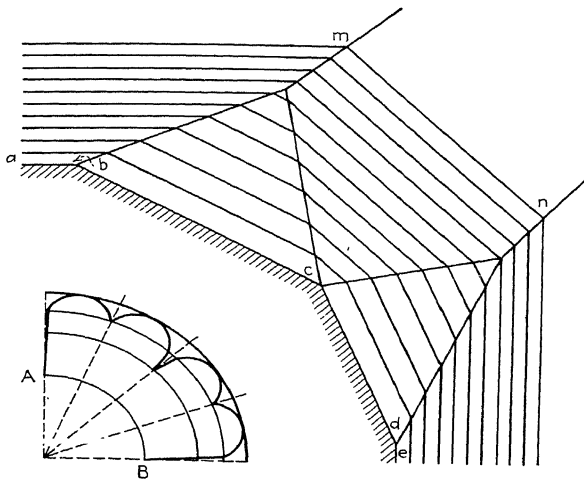


FIG. 25.—Change in outline of crystal during growth due to different growth velocities of various faces. (From C. H. Desch, "Chemistry of Solids"; Cornell University Press.)

This variation in growth velocity is, of course, dependent upon the different atomic arrangements in the various directions. Figure 26 shows the structure of (100), (110), and (111) planes of sodium chloride. The octahedral direction is made up of planes of ions of the same sign, planes of chlorine ions alternating with planes of sodium ions. The cube is made up of a checker-board pattern of ions of the opposite sign. There is at least a 50 per cent chance of an ion being attached to the (111) plane because the only requirement that must be fulfilled is that it be of the opposite sign. However, the chances of an ion adhering to the cube plane are considerably less because the ion must be of the right sign and it must also impinge at the correct place in

order that it may be attracted. Hence the growth velocity of the cube is less than that of the octahedron, and the dominant habit of pure sodium chloride is cubical and not octahedral.

Experimental evidence shows that under ideal conditions, all faces of a crystal having but a single form grow at the same rate regardless of the original sizes of the individual faces. If a crystal has a number of forms, like faces (*i.e.*, faces of the same form) grow at the same rate but unlike faces grow at a different

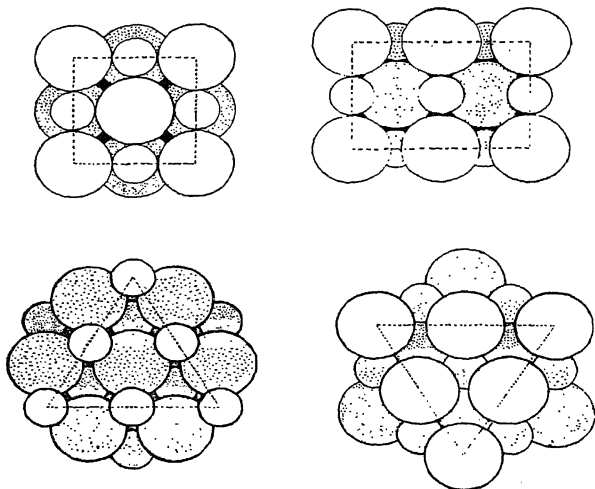


Fig. 26.—Atomic arrangement of sodium chloride. *a* (100); *b* (110); *c* and *d* alternate planes (111). (*Rinne*,⁽¹⁶⁾)

rate. The rate of growth of parallel faces of a crystal without a center of symmetry may be different and faces adjacent to larger faster growing faces may be slowed up owing to the impoverishment of the solution in the neighborhood of the slower growing faces.

Crystals can be grown by the condensation of vapor on solid surfaces. If the temperature of the surface is sufficiently low, an amorphous solid may be formed. There is a greater chance to form crystals if the temperature of the surface is raised, the optimum temperature being dependent on the nature of the substance. It is also preferable to use a solid of the same material

or one having a similar crystal structure, since the impinging atoms will have a greater tendency to orient themselves. The growth of crystals in this manner is of considerable interest; but, since it does not have direct application in refractories, it will not be discussed further.

Little is known of the crystallography of colloidal and microscopic crystals. In comparison with macroscopic crystals, the surface forces are tremendously greater owing to their larger specific surface and hence play a much more important role in determining the properties of such crystals. It is interesting to note that the habit of these small crystals is often considerably different from that of larger crystals of the same compound. These small crystals usually have a greater variety of faces than the larger crystals; but, if they were permitted to continue growth, their habit would eventually become the same as that of the larger crystals. The forms observed on crystals are not necessarily the equilibrium ones but are dependent in a complex way on the nature of the surface forces, impurities in the solution, and other factors.

We can conclude from the preceding discussion that crystals grow by the accretion of matter on their outer surfaces in such a way that there is an exact dovetailing between the structure and magnitude of the surface force field of the crystal and the atoms or atomic groups being attached to it. Therefore, crystal growth may be described as the attachment of an atom or group of atoms to the growing crystal surface in a manner to make the free energy of the surface a minimum. The change of energies involved is complex, and the reader should consult Desch⁽⁵⁷⁾ and Kossel⁽²⁴⁾ for details.

The successive addition of positive and negative ions to incomplete rows . . . of . . . a crystal . . . is always accompanied by the same change of energy. . . . It includes energy liberated by the attachment of the ion in a stable position in the lattice, less than needed to remove the ion from the attached solvent. Some degree of polarization of the ions may also occur. The energy of dehydration is about equal to that liberated by the attachment of an ion. . . . (57, pp. 36-37)

The planes that have the greatest chance of becoming permanent faces of the crystal and are the most common are those normal to the directions of least growth velocity.

Before leaving the problem of crystal growth, mention should be made of *mineralizers*. Granites and pegmatites crystallize at comparatively low temperatures (500 to 600°), but these are far above the critical temperature of water. Laboratory studies show that melts of granite composition are extremely viscous; therefore small crystals or glass would be expected to form. We know, of course, that these rocks are made up of large crystals (in contrast to a rhyolite). Many years ago, it was shown that small amounts of mineralizers, particularly water, were present in the magma. They promoted fluidity causing coarse-textured rocks with large crystals to be developed. The mineralizers may

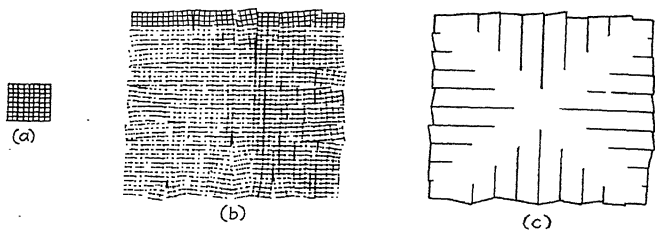


FIG. 27.—Two dimensional (idealized) lattice of perfect crystal *a*, actual crystal, lineages *c*. (From M. J. Buerger, *Z. Krist.*)

or may not enter into the chemical composition of the minerals. Water is the most important and abundant of the natural mineralizers, and H_2S , HF , CO_2 , some titanium compounds, borates, phosphates, and others are known to be active as mineralizers. The early French chemical school used mineralizers as aids in the synthesis of silicates (see Fouque and Levy⁽¹⁾ and Morozewicz⁽²⁾ who used tungstates).

Lineages.—A careful examination of crystals shows that they are rarely perfect. Even crystals of lithium fluoride grown in Stockbargers' elaborate apparatus under the most carefully controlled conditions are not perfect, as can be readily verified by the roughness of a cleaved surface. An ideally perfect crystal would have a lattice whose points all fell on straight continuous parallel lines, as shown in Fig. 27*a*. Probably the only crystals that attain such ideal perfection are submicroscopic in size. In macroscopic crystals, the lattice is discontinuous and branched (Fig. 27*b*). M. J. Buerger has used the term "lineage" for each of the continuous branches of the lattice. Each major

lineage may be subdivided into sublineages which, in turn, may be split. Crystals consist of a host of such lineages, each one oriented slightly differently but almost parallel to its neighbor and all growing in a somewhat dendritic fashion from the original nucleus of the crystal. Figure 27c shows a single hypothetical crystal composed of a number of lineages extending from the center of the crystal. These lineages do not, however, form a



Fig. 28.—Cleavage surface of galena showing lineages, (7×). (From M. J. Burger, *Z. Krist.*)

regular systematic secondary structure in crystals.⁽⁵⁵⁾ Each lineage has its own termination; and, in extreme cases, the surface of the crystal takes on a stepped or mosaic appearance. Figure 28 shows the marked irregularity, due to lineage structure, of a cleavage surface of galena.

Lineages form early and persist until the growth has been nearly completed. In general, they grow faster in a particular direction, and later sublineages appear. The nature of the lineages is apparently dependent upon the rate of cooling, type of compound, impurities, shape of the container, and other factors. The interstitial material crystallizes last in the voids between the lineages. Lineages of Al_2O_3 grown from a melt are

shown in Fig. 29. Here each of the lineages is made up of parallel growths of crystals with faces that are already well developed. Similar phenomena take place in metals and in crystals grown from solution. Lineages and other imperfections are apparently a universal characteristic of most crystals, and "perfect" crystals are indeed rare.

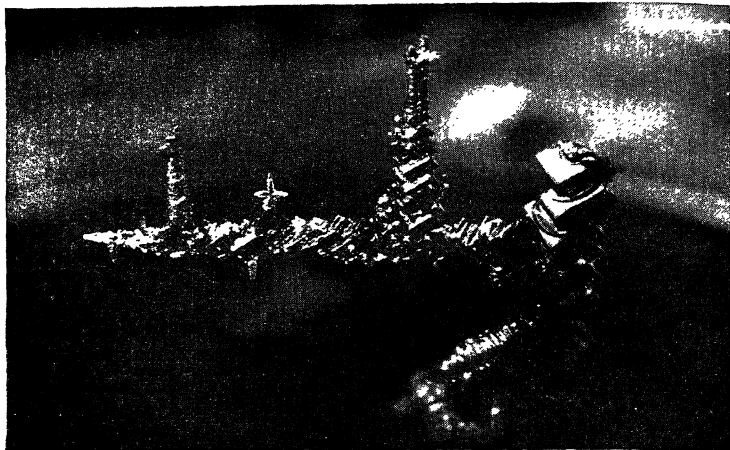


FIG. 29.— Al_2O_3 dendrite grown from melt, showing lineages, ($5\frac{1}{2}\times$). (From M. J. Buerger, *Z. Krist.*)

The discontinuities between the lineages are often the locus of voids in the crystal and may contain gases or liquids characteristic of the mother liquid. The boundaries may also afford a better opportunity for replacement and exsolution phenomena than the lineage itself. These voids may lead to an incorrect determination of the density; consequently it is always necessary to break the material into small particles in order to obtain better values. Lineages may also introduce boundary effects into conductivity measurements, but this has not been investigated. Lineages are a cause of variation between computed and measured intensities of X-ray reflections and also cause the reflections to be spread over a small area instead of forming a sharp spot. Smekal⁽⁵⁰⁾ has developed a comprehensive theory of the effect of flaws ("lockerstellen") on the properties of crystals and

The presence of these flaws in real crystals makes it extremely difficult to predict the strength, electrical conductivity, and other properties from calculations based on ideal crystals. The well-known case of sodium chloride having a considerably lower strength than that calculated on the basis of interionic forces in the lattice of an ideal crystal is a good example.⁽²³⁾

Crystal Habit Variation.—The “habit” of a crystal is a broad term describing the relative sizes, shapes and number of faces, or the general shape and form of a crystal. The habit of crystals

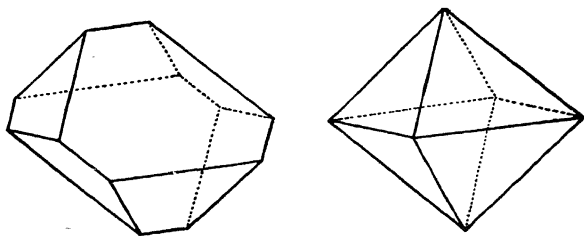


FIG. 30.—Malformed alum crystal (left) grown on bottom of beaker and perfect crystal grown by suspension. (From A. F. Rogers.)

of the same compound grown under similar conditions from solutions of the same purity is usually the same. Thus crystals from the same locality or prepared in the laboratory under the same conditions generally have the same habit. However, if the purity of the solution or conditions of growth are varied, the habit usually shows corresponding variations. It should be kept in mind in the following discussion that as a result of the regular atomic arrangements, Steno's law is obeyed. We shall first take up briefly the habit of pure compounds and then discuss habit variation due to impurities in the crystallizing medium.

We are familiar with the fact that similar faces of crystals rarely have the same size and shape. The shape and size of the container in which the crystals are grown, rate of cooling, and number of nuclei all play a role in determining the amount of distortion. For example, crystals of alum formed on the bottom of a beaker are flattened, whereas those suspended in the solution and growing unimpeded form more perfect octahedra (Fig. 30). The rate of cooling may also profoundly alter the habit. If the crystals are grown too rapidly, certain faces that would normally

develop may never have an opportunity to grow to any appreciable size. Crystals of KMnO_4 grown slowly by evaporation develop a dominant macrodome {102}; but, when the crystals are grown more rapidly, there is a tendency for the development of prismatic crystals elongated parallel to the b -axis (Fig. 31*b*).

If impurities are present in the solution, they may be incorporated in the crystal in solid solution, they may be adsorbed by

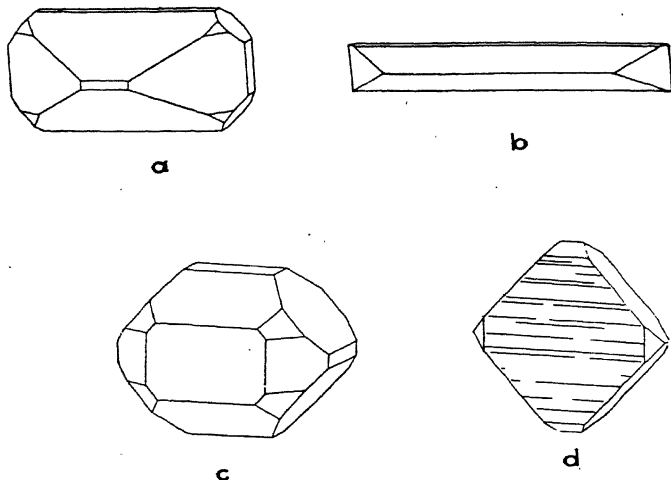


FIG. 31.—Crystal habit-variation of KMnO_4 . (*a*) Crystals grown slowly by evaporation, macrodome {102} dominant; (*b*) crystals grown rapidly, prismatic, elongated parallel to b -axis; (*c*) grown with dilute concentrations of K_2CO_3 ; (*d*) grown with equal ionic concentration of K_2CO_3 . *H. E. Buckley, Z. Krist.*)

a number of forms or only by a particular form of the growing crystal, or there may be no adsorption of the impurity. The factors that determine which will take place are the similarity between the force fields, structure, polarizability, etc., of the surface of the crystal and that of the impurity.

The case of lead nitrate crystallizing from a solution containing methylene blue vividly illustrates the selective nature of adsorption. The normal habit of pure lead nitrate grown from a water solution is octahedral; but, if a small quantity of methylene blue is added, the crystals develop small cubic faces truncating the octahedron. The octahedral planes are colorless, whereas the

cube faces are blue. As the concentration of the dye is increased, the cube faces become more prominent and finally, with a certain concentration of dye, only cubes are obtained. In other words, the growth vector of $\{111\}$ decreases and that of $\{100\}$ increases with increasing amounts of dye.

It can be seen that this phenomenon is due to the *selective adsorption* of the dye by the $\{100\}$ planes whereas the $\{111\}$ planes are not affected. Buckley,⁽³³⁾ however, has shown that the simple picture presented here is not wholly correct. The "cube" planes are (110) , and the complex structure of the dye makes the interpretation more involved. Nevertheless, the general idea is correct in principle, if not in detail, and a more precise description is given in his paper. The selectivity is due to the fact that the atomic structure of lead nitrate on the $\{111\}$ surfaces is different from that on the $\{100\}$ surface and conditions in the latter are more favorable to housing the dye. The dye therefore acts as a protecting blanket, slowing up or preventing the normal accretion on $\{100\}$. Consequently the growth velocity in this direction is reduced; the cube faces persist at the expense of the faster growing octahedral faces; and the habit becomes cubical rather than octahedral.

The classic example of urea changing the crystal habit of sodium chloride from cubical to octahedral is also explained by the selective adsorption of urea on the octahedral planes. A further example of the marked effect of the concentration of the impurity on the habit of crystals is illustrated by KMnO_4 crystals with dilute K_2CO_3 (Fig. 31c) and with equal ionic concentrations of K_2CO_3 (Fig. 31d). For a more complete description and analysis of the relationship between selective adsorption and crystal-habit modification, the papers by Buckley,⁽⁵⁴⁾ and Frondel⁽⁶⁰⁾ are recommended.

The selective nature of crystal adsorption may be of practical importance in the synthetic coloring of crystalline materials. We have seen that, unless there is some similarity in structure of the coloring matter and that of the crystal, no adsorption will take place. Moreover, the color of crystals is often unequally distributed in segments or bands depending on the nature of the coloring material.

Oriented Overgrowths and Intergrowths.—Oriented overgrowths are vividly shown in the photomicrographs of Fig. 32, from Bunn.

On the left are ammonium iodide crystals grown on a glass surface. Since there is no regular repeat period in the atomic arrangements of glass, the crystals grow with a random orientation. The photograph at the right shows the same crystals grown on a freshly cleaved mica (muscovite) surface. Here each crystal has a parallel orientation due to the vectorial forces exerted by the mica sheet on the growing crystals. Oriented overgrowths have been observed in a number of minerals (rutile on hematite, chalcopyrite on sphalerite, etc.), and the orienting

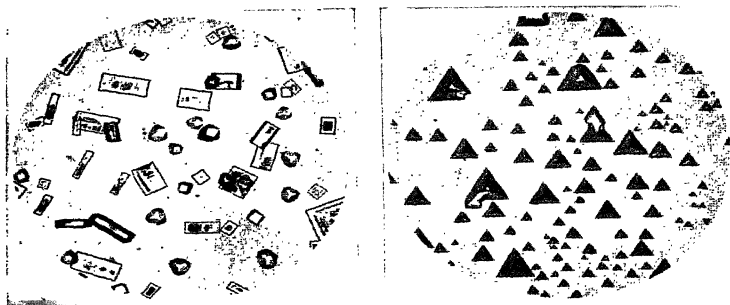


FIG. 32.—Crystals of NH_4I grown on glass (left) showing random orientation and on layer of muscovite (right) showing preferred orientation. (From W. L. Bragg, "*Atomic Structure of Minerals*"; George Bell & Sons, Ltd.)

influence of the substrate on the superdeposited mineral is dependent on the similarity of their structures. When the superdeposited crystals and the substrate have planes with similar atomic arrangements and force fields, there is a tendency for a preferred orientation. Hence, if the ammonium iodide crystals were grown on another crystal that did not have a similar atomic arrangement, there would be no tendency for preferred orientation. Instead, they would be random just as in the case of glass. It is interesting that a piece of glass polished in one direction assumes a certain surface anisotropy. Zocher⁽²⁷⁾ proved this by showing that methylene blue crystals grown very rapidly on such a surface were oriented, as indicated by their polarizing power. We shall see later that a similar phenomenon takes place in intergrowths. For further data, see recent papers by Frondel,⁽⁶⁹⁾ which are recommended for clarity.

Another example of the influence of adsorption at the crystal-solution interface is found in the *selective incrustation* of minerals.⁽⁶⁸⁾ In the crystallization of certain minerals in an open space in the presence of various earlier formed crystals of different species, there is a tendency for the later mineral to crystallize preferentially on a particular species instead of encrusting all species. In these cases, chemical reaction between the solution and the surface of the crystal may also affect the selec-

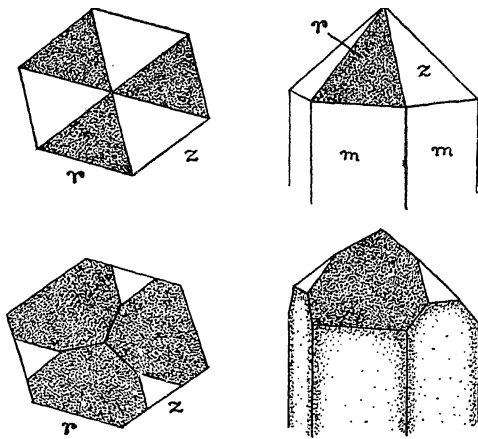


FIG. 33.—Selective incrustation of crystal forms. Hematite (stippled) on quartz, Paterson, New Jersey; r = positive rhombohedron, Z = negative rhombohedron, m = prism. (From C. Frondel, *Am. Mineral.*)

tivity. Thus minerals with similar crystal structures have a marked tendency to encrust each other, whereas quartz and the metallic sulfides (which are not similar structurally) show no such tendency.

A careful examination of the encrusted minerals shows that a particular form or group of forms of certain crystals are covered with a superdeposited mineral whereas other forms of the same crystal are not. This is illustrated in Fig. 33, from Frondel. Here the positive rhombohedron of a quartz crystal from Paterson, New Jersey, is covered with a film of bright red hematite but the negative rhombohedron is not covered. Moreover, the prism is not so heavily encrusted as the positive rhombohedron; and, in

addition, the corners and edges of the prism are more heavily encrusted than the face. This can be interpreted on the basis that the adsorptive power of the different forms of quartz is variable. In this particular case (*i.e.*, hematite encrusting quartz), the adsorptive powers in decreasing order are positive rhombohedrons, prism corners and edges, and prism faces, whereas the negative rhombohedrons are not coated and apparently exhibit no attraction for the hematite.

Lastly, mention should be made of exsolution intergrowths. The crystallization of a substance from solid solution in another crystal is similar in principle to the overgrowths described above. In exsolution, the crystals of the precipitated phase tend to orient within the host crystal so that structurally similar planes in the two substances coincide. In this way, the expenditure of energy for the generation of the new surface is kept at a minimum. Well-known examples are ilmenite and magnetite mutually exsolved from solid solution so that (0001) of the former is parallel to (111) of the latter (these planes are the most similar of the two structures) and to ilmenite and hematite shown in Fig. 34. At high temperatures, potash feldspar and soda-lime feldspars are miscible to a certain degree; and, as the temperature falls, the latter may crystallize out as oriented inclusions in the host crystal to form a "perthite."

5. Identification of Crystals. *X-ray Analysis.*—There are so many applications of X-ray methods in the field of ceramics that only a few of the more obvious uses can be pointed out here. With experience, the X-ray analyst develops many techniques and uses for his specific problems. In brief, it is perhaps the most useful analytical method available for the study of matter in the solid state. However, as is true with other methods of analysis, it has its limitations; for no one method is complete in itself, and supplementary data obtained by other methods are desirable and often necessary. This method of analysis has many advantages over others because the specimen is examined as it is, without changing its condition or state of chemical combination in any way. In addition, the method works equally well for opaque and nonopaque materials and on grains far smaller than those necessary for petrographic methods. The X-ray method is used mainly for the study of crystalline solids, although the work of Warren shows that much information can be obtained from

glasses. Perhaps the most useful application of the method is in the identification of crystalline solids, mixtures, solid solutions, etc. It will readily distinguish between crystalline and glassy matter and thus can be used to detect devitrification in glasses. Since the results obtained are dependent upon the actual arrangement of the atoms, they are less affected by superficial variations than by most other methods. By the same token, many minute but significant variations can be detected and certain

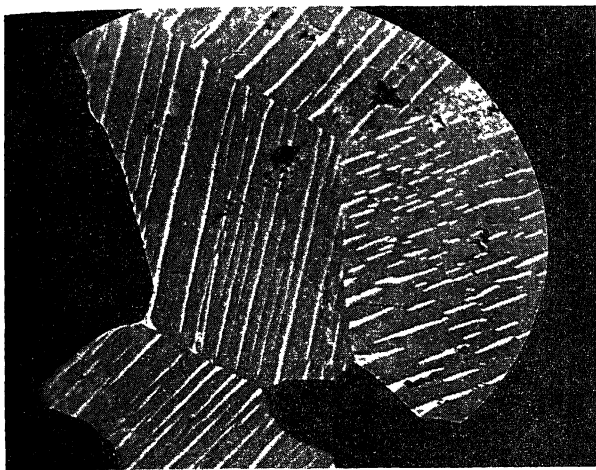


FIG. 34.—Hematite (light) and ilmenite (dark), exsolution intergrowth, Schroon Lake Village, N. Y. (200 \times). (*W. H. Newhouse, Bul. Geol. Soc. Am.*)

important information that cannot be got by other methods can be obtained by X-ray analysis.

As little as 1.0 mg. of the sample, which may be in the form of a powder, is required for an X-ray analysis. If only a small amount of sample is available it may also be used for other analytical methods or retained for records, since it remains unchanged by the examination.

There are many miscellaneous applications of the X-ray method such as following the course of chemical reactions; learning the effect of heat-treatment at various stages; detecting grain growth, recrystallization, and phase change; determining particle

sizes of microscopic and submicroscopic grains (Chap. XIX); and measuring thermal expansion (Chap. XVI), preferred orientation, and strain.

The most important method for identification by X-ray analysis is the "powder method." A fine beam of monochromatic

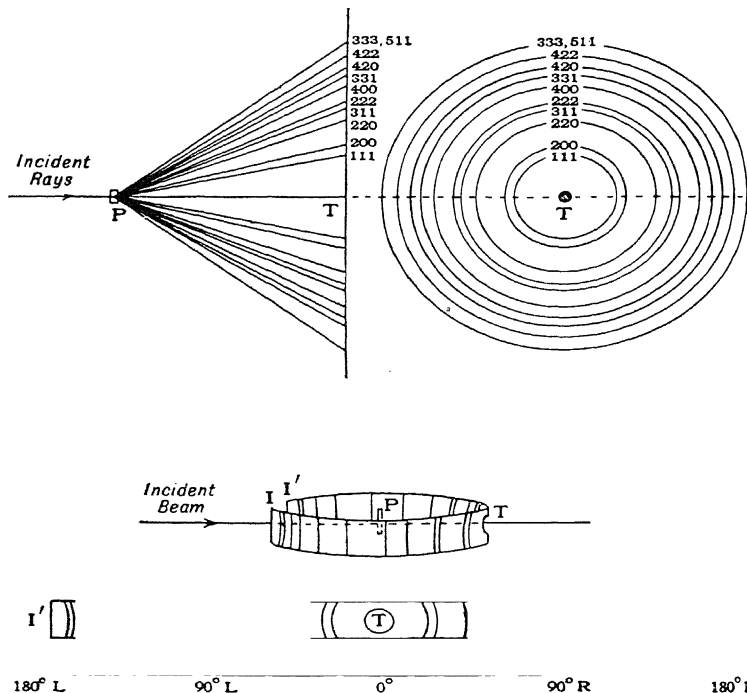


FIG. 35.—Powder photographs on a flat plate (above) and cylindrical film (below). (From W. L. Bragg, "The Crystalline State"; The Macmillan Company.)

X rays strikes a small amount of powder in which the crystals have a random orientation. The interatomic distances are about the same as the wave lengths of the X rays, so diffraction takes place according to the Bragg equation

$$n\lambda = 2d \sin \theta$$

where n = an integer (usually one in powder pictures)

λ = the wave length of X rays used

d = the distance between atomic planes

θ = the diffraction angle

The diffracted X rays are recorded on either a flat or a cylindrical film, as shown in Fig. 35; and Fig. 36 shows a number of typical photographs. The spacings and intensities of the lines are dependent upon the atomic arrangement and composition of the crystal; therefore the pattern thus formed serves as an absolute means of identification, for no two compounds give the same pattern. For details of this method, the reader should consult Davey⁽⁵⁶⁾ or Wyckoff.⁽⁷¹⁾

In order to find the mineral corresponding to a given pattern, some form of indexing is needed. This is especially true when several minerals occur in the same sample. One of the most important advances in the identification of compounds by the powder method is that of Hanawalt, Rinn, and Frevel.⁽⁹⁴⁾ They give the spacings and intensities of the lines of 1,000 chemical substances and describe a method for identifying the compound by use of an elaborate catalogue (462 pages) which can be compiled easily from their data. The spacings of all the substances vary from 0.5 to 20 Å. and are divided into 77 major divisions (based on the d values of the strongest line of each pattern), which, in turn, are subdivided into 77 subgroups (based on the spacing of the second strongest line). The sizes of the divisions are based upon experience and are larger than the accuracy of the measurement of the positions of the lines. The name of the compound and d values of the third and fourth strongest lines are also included in the catalogue. With each major division is a supplementary group index section, giving the names of all the compounds whose strongest line falls in that major division and also the three strongest lines listed in three orders: 1, 2, 3; 2, 1, 3; 3, 1, 2. A compound can be identified by measuring the positions and relative intensities (visual) of all the lines on the film and listing them in order of decreasing d . Attention is then fixed on the three strongest lines, which can be picked out easily with some experience; if two lines have the same intensity, the rule is to list the one with the greater d value first. The strongest line determines the major group, and the second strongest line the subgroup in the catalogue. Most subgroups contain only one

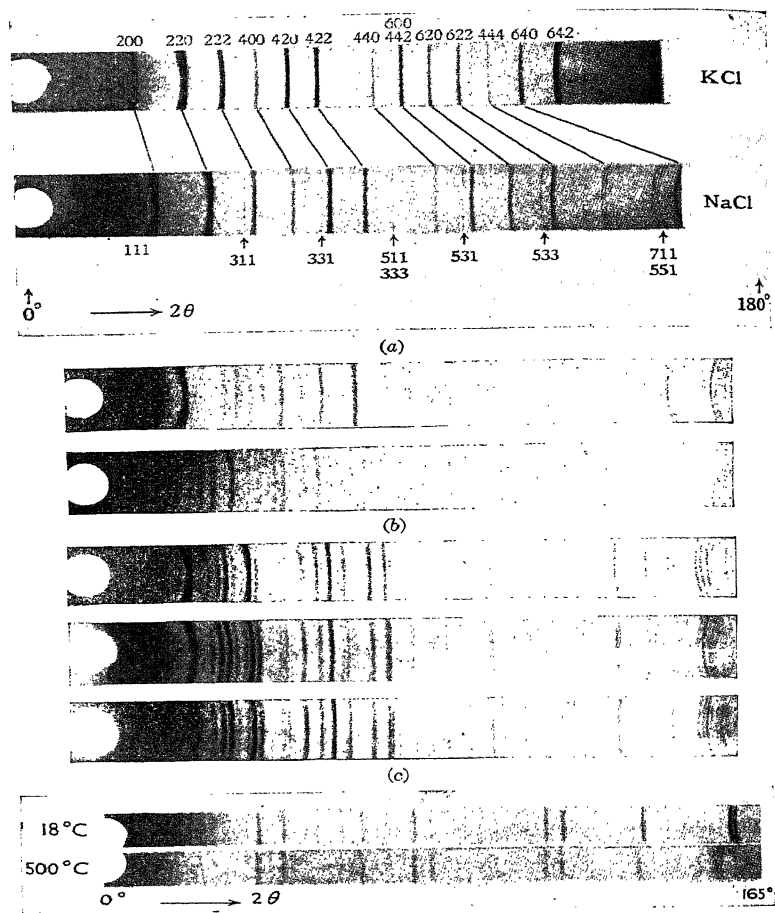


FIG. 36.—Powder photographs on cylindrical films. (From W. L. Bragg, "The Crystalline State"; The Macmillan Company.) (a) KCl (above), NaCl (below) showing indices of corresponding planes. (b) Quartz (above) and cristobalite (below) give totally different types of patterns. (c) Aluminosilicates. These are similar in composition and structure but can be differentiated by powder pictures especially in the high Θ regions (far right) of the film. (d) Silver at 18° (above) and 500°C (below). Thermal expansion is shown by shift of lines toward center of film, indicating a larger lattice parameter.

compound (the largest number in the subgroups is seven); consequently if the third strongest line checks with one of the compounds listed, the identification is completed. The fourth line can be used as additional evidence, and the original known film can be used for final evidence. If no match is obtained, valuable negative evidence has been secured during the search.

If the unknown is a mixture of phases and if the second strongest line of the pattern happens to be the strongest line of the second component, the pattern will not have been found and one proceeds by using the third strongest line of the unknown pattern to determine the subgroup, and so on. One cannot fail to find any or all the components of a mixture which exists in the reference file.⁹⁴

Thus the method works like a fingerprint file, and any compound listed in the catalogue can be identified rapidly. The original paper should be consulted for the routine of identifying mixtures containing components with some superimposed lines.*

If only a limited number of substances, say 150 at most, is all that one will reasonably expect to find in some specialized field, the method suggested by Warren⁽⁶²⁾ should be most helpful. First, a little library of known patterns is compiled from carefully selected samples, preferably those with a chemical analysis. The voltage, exposure time, amount of sample, developing, etc., should be kept as constant as possible. The films are measured, and all the lines of each substance are listed in order of decreasing spacing. The intensity and index of the line, if known, should also be listed. It is advisable to check the measured values with those in the literature^(94,21) or with the spacings as determined from the indices, if the film can be indexed; if the structure of the compound is known, the computed spacings and intensities

* A 4,000-card index of X-ray diffraction data is now available from The American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. Supplementary cards will be issued as new data becomes available. See also *Am. Mineral.*, **27**, 63-113, 1942. A recent Russian publication gives an enormous amount of data but may be difficult to obtain: Mikheiev, V. I., V. N. Dubinina, and G. A. Kovalev, *Ann. de l'Institut des Mines à Léninograd*, **11**, II, 1939; Boldyrev, A. K. V. I. Mikheiev, and G. A. Kovalev, *ibid.*, **13**, I, 1939. For indexing films see also *J. Applied Phys.*, **8**, 553, 1937; *ibid.*, **13**, 109, 1942; *Am. Mineral.*, **26**, 395, 1941. Additional data may be found in issues of *Am. Mineral.*, *Mineralog. Mag.* (London), *Z. Krist.*, *J. Chem. Phys.*, *J. Am. Chem. Soc.*, *J. Am. Ceram. Soc.*, *Univ. Toronto Studies, Geol. Ser.*, issued annually, etc.

can be compared with the measured values. Although the catalogue of spacings could be compiled directly from the literature, it is good practice to have the films of the knowns available for direct comparison. A catalogue is then compiled with the spacings of *all* the lines of *all* the compounds arranged in order of decreasing d with the intensity and the name of the compound listed with the line. Such a list would cover many pages but

TABLE 13.*—SAMPLE CATALOGUE OF SPACINGS AND INTENSITIES OF DIFFRACTION LINES OF SIX COMPOUNDS FOR RANGE $d = 1.750$ TO 1.350

d	I/I_1	Compound	d	I/I_1	Compound
1.74	0.50	α -Al ₂ O ₃ †	1.53	0.04	α -Cristobalite
1.72	0.07	Muscovite‡	1.50	0.05	α -Al ₂ O ₃
1.69	0.05	α -Cristobalite§	1.498	0.33	Muscovite
1.67	0.40	Kaolin	1.494	0.06	α -Cristobalite
1.66	0.08	α -Quartz¶	1.490	0.56	Kaolin
1.64	0.20	Muscovite	1.450	0.02	α -Quartz
1.63	0.08	MgAl ₂ O ₄ **	1.430	0.05	α -Cristobalite
1.51	0.12	α -Cristobalite	1.417	0.75	MgAl ₂ O ₄
1.69	1.00	α -Al ₂ O ₃	1.402	0.40	α -Al ₂ O ₃
1.57	0.01	α -Cristobalite	1.400	0.02	α -Cristobalite
1.54	0.40	MgAl ₂ O ₄	1.375	0.25	α -Quartz
1.54	0.20	α -Quartz	1.370	0.50	α -Al ₂ O ₃
1.54	0.16	Kaolin	1.370	0.03	α -Cristobalite
1.54	0.05	α -Al ₂ O ₃	1.358	0.01	MgAl ₂ O ₄

* Table compiled from data given by Hanawalt, Rinn, and Frevel.⁽⁹⁴⁾

† [Their] Pattern No. 11.

‡ Pattern No. 16.

§ Pattern No. 745.

|| Pattern No. 17.

¶ Pattern No. 746.

** Pattern No. 497.

still be smaller than the catalogue required by the Dow method described above. d would probably vary from about 0.2 to 20 Å. as in the Dow tables. A sample list covering the range $d = 1.750 - 1.350$ for α -Al₂O₃, muscovite, α -cristobalite, kaolin, α -quartz, and MgAl₂O₄ is given in Table 13. Identification is then easy and rapid. The film of the unknown substance is measured; spacings are computed and compared with those of the catalogue. For each spacing value of the unknown, the possible substances that have the same spacing within experimental error would be listed in the catalogue. Thus, if the unknown showed lines $d = 1.74, 1.59, 1.54, 1.50, 1.402$, and 1.370 in the range

covered by Table 13, the mineral would be $\alpha\text{-Al}_2\text{O}_3$. The larger the catalogue the greater the possibility for two or more compounds to have one or more lines in the pattern with identical spacing, but the chance of identification is also greater. There are four compounds in Table 13 with $d = 1.54$ and two with

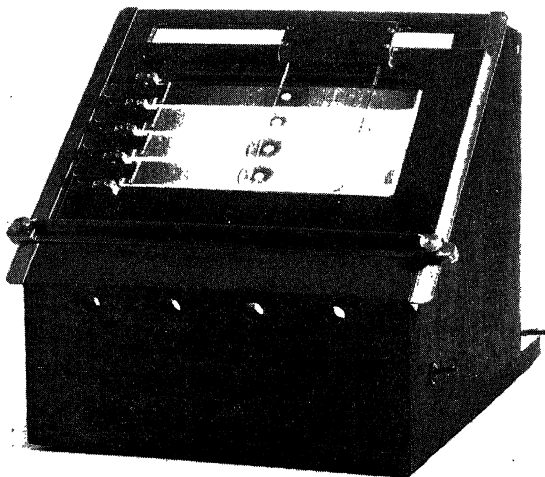


FIG. 37.—Device for comparing powder films. (Courtesy of M. J. Buerger.)

$d = 1.370$. In general, the number of coincidences of d values of different compounds is small. Also most of the remaining lines apparently will have different d values, and hence identification is assured provided the substance is listed in the catalogue. If the unknown has been identified with the catalogue or limited to two or three possibilities, the unknown is compared with the original patterns and checked carefully for intensities as well as spacings. A device for comparing spacings of a number of powder films is shown in Fig. 37. Absolute intensity comparisons are not necessary. Such a catalogue of crystalline ceramic substances would be most useful.

Clark⁽¹¹⁵⁾ gives a good review of the various types of X-ray apparatus. In general, it is expensive, and the price varies

considerably depending upon the type of equipment. A moderately complete X-ray laboratory probably cannot be set up for less than about \$3,000, which is very likely the minimum.

There are two principal types of X-ray tubes: the gas or ion type and the electron type, which has a permanent vacuum. The life of the former is practically unlimited; different types of targets can be introduced readily; and it is the type best suited for general X-ray work. The electron-type tube (often called "filament tubes") are easier to handle but have a limited life—usually about 1,000 hr. Excellent filament tubes with various targets can be purchased in this country, and gas tubes can be made up in a shop or purchased.

Unlike microscopic equipment, which is well standardized, X-ray equipment is, in many respects, still not in the "push-button" stage. It is absolutely necessary to consult with *two or three* experienced X-ray analysts before placing an order. A remarkable improvement in X-ray apparatus is the new General Electric unit (Fig. 38), which is as near a foolproof unit as can be obtained commercially at the present time. The company supplies excellent data on operation⁽¹²⁵⁾ and will arrange for installation, so even a man with little experience can operate it successfully. A number of universities are now training men in X-ray diffraction analysis. It is unreasonable to expect a man with no formal training in this field to be able to use the method to its fullest advantage. On the other hand, a man trained only in X-ray technique and with no background in the crystal chemistry of the solid state could not derive the full benefit and power of the method. Of course, much equipment can be built, but it is not advisable unless a well-equipped shop and an instrument maker experienced in the construction of X-ray equipment are both available.

Dangerous burns may result from improper handling of X-ray equipment. Before the equipment is used, an experienced X-ray analyst and the directions of the National Bureau of Standards should be consulted. Modern X-ray equipment can be used easily with complete safety if handled properly and if minimum precautions are followed.

Petrographic Analysis.—The study and identification of minerals with the petrographic microscope is a science that has been developed to a high degree and is now an indispensable tool in

many types of investigations. Petrographic methods can be used in identifying fragments smaller than the head of a common pin even if only minute quantities are available. Moreover, the grains need not have crystallographic faces. Men who have had a few college courses in the subject can, with experience, develop

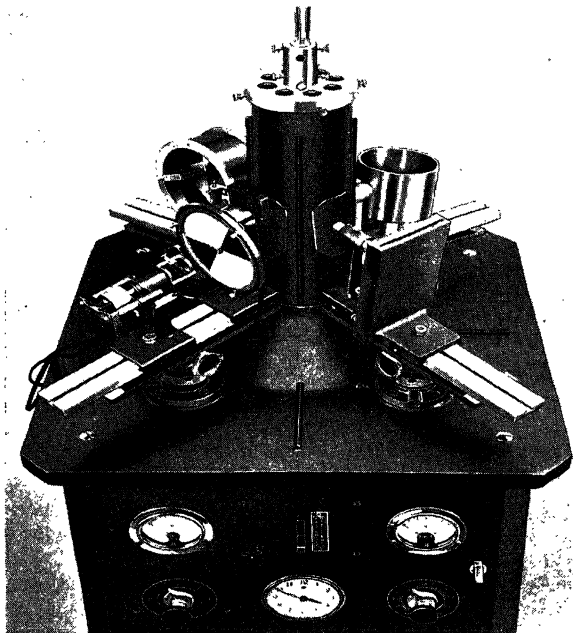


FIG. 38. —The new General Electric XRD unit with four types of cameras in place.⁽¹²⁵⁾

into competent petrographers. The technique is simple, does not require very elaborate apparatus, and has a number of distinct advantages over other methods.

The identification of chemically complex minerals by petrographic methods is no more difficult than that of chemically simple compounds. A silicate analysis may take an expert chemist four or five days, but identification by the immersion method can be made in an hour or less, thereby permitting a large

saving in time and money. The identification of various phases of the same compound (polymorphs) are as easily distinguishable as two different compounds. Thus a chemical analysis of a chrome ore before and after firing would not show the effect of the heat-treatment, whereas an optical study would show the phase and textural changes that have taken place. A good example is found in the firing of silica brick. Chemical analysis would not distinguish between the phases of silica developed, but petrographic analysis would show the relative amounts of quartz, tridymite, cristobalite, and glass.

In addition, the degree of homogeneity of the material can be readily observed; mixtures are easily distinguished; and their individual components identified. For example, a mixture of corundum ($n = 1.760 - 1.768$) and mullite ($n = 1.638 - 1.653$) can be immersed in a liquid of refractive index $n = 1.70$, and each readily distinguished by a simple central-illumination test in a matter of a few minutes.

Another example will illustrate how petrographic studies are useful in supplementing chemical data. A chemical analysis of sand for making glass would show, let us say, the exact amount of iron oxide and titania present. But this does not reveal whether the impurities are present as limonite coating the quartz grains or as single crystals of ilmenite and magnetite. This knowledge, necessary in order to know which procedure should be employed to purify the sand, can be obtained from petrographic study.

It should not be inferred from the preceding discussion that petrographic methods have taken or will take the place of chemical analysis. Both methods have their sphere of usefulness. It should be emphasized that petrographic procedure, and especially the immersion method, is probably the best method for the identification of nonopaque minerals. Perhaps the most serious drawback of the method is that, if the grains are smaller than about 300 mesh, identification may be difficult or impossible.

Petrographic techniques have attained such importance in the field of ceramics that the entire February, 1937, issue of the *Bulletin of the American Ceramic Society*⁽⁸⁶⁾ is devoted to a bibliography of papers dealing with various phases of ceramic microscopy.

A great wealth of information can be obtained from the microscopic examination of a thin slice of the specimen (0.03 mm. thick)

mounted on a glass slide with Canada balsam. Although the indices of refraction cannot be determined accurately, they can be estimated and the other optical properties determined. More experience is required on the part of the investigator than for identification by the immersion method; but identifications can be made readily, and one soon becomes familiar with the common minerals that have characteristic properties just as in the case of hand specimens. One of the great advantages of thin sections over the immersion method is that the texture and intimate relations of the constituents can be readily observed exactly as they exist in the specimen. In this way, a study directly at the interface can be made of the effect of the melt on the refractory. The study of thin sections is described in the standard textbooks and the recent paper of Faust and Gabriel.⁽¹¹⁸⁾

The composition of the specimen in terms of the percentage of each mineral can be determined by thin-section studies. The section is moved through the field of view by an integrating stage attachment, and the distance occupied by each mineral is registered by a mechanical or electrical counter.⁽¹⁰⁵⁾ The apparatus usually has five or six counters—one counter for each mineral and one for empty spaces. After a number of traverses are made across the section, the percentage of each mineral can be computed from the areas that, in turn, are obtained from the distances registered on the counters. It is necessary to be able to identify the minerals rapidly, for otherwise the time required would be prohibitive. Usually they can be identified at sight; but at times a rapid distinction between, say, feldspar and nepheline is difficult. Keith,⁽¹⁰⁷⁾ Shand,⁽¹¹⁰⁾ and Faust⁽¹¹⁷⁾ recommend methods for distinguishing such minerals in which the sections (without cover glasses) are exposed to an acid and then stained by dyes. In this way, one mineral may be stained, say, green and the other another color or may remain colorless. Then the minerals can be rapidly identified, and the Rosiwal analysis computed.

A number of books are available that give a comprehensive discussion of the theory and methods of optical mineralogy. The books of Buchwald,⁽⁸³⁾ Buerger,⁽¹⁰²⁾ Chamot and Mason,⁽¹¹⁴⁾ Groth,⁽⁵⁾ Johannsen,⁽¹¹⁾ Niggli,⁽¹⁵⁾ Winchell,⁽⁹⁸⁾ and Wright⁽⁶⁾ are recommended.

The principal refractive indices and their crystallographic orientation are the most fundamental optical constants of the mineral. The birefringence, optic sign, and optic axial angle can be computed from the indices and can be also determined directly. The measured data can then be used to check the computed data. Additional data such as dispersion of the optic axes, extinction angle, and pleochroism can be readily determined by the well-known methods. A brief review of the examination by optical methods is given in Fig. 39.

The most complete discussion of the immersion method, which has been found so useful for identification purposes, is that of Buerger.⁽¹⁰²⁾ It should be emphasized that although the immersion method is one of the most useful means for identifying non-opaque minerals and can be applied to many types of problems, its full value cannot be realized without a good background in optical crystallography. It is of little practical use to know how to determine the refractive index of an anisotropic mineral to four decimal places if the orientation of the grain is unknown.

The immersion method resolves itself into finding a liquid whose refractive index is the same as that of the mineral. A series of standard liquids of known refractive index are used for this purpose and are described by Kaiser and Parrish.⁽¹⁰⁶⁾ After the indices have been measured, the mineral may be determined by the use of the tables prepared by Larsen and Berman.⁽⁶⁸⁾ These tables are the best available and are invaluable in routine identification by the immersion method. The determinative tables of Winchell⁽⁶³⁾ and his descriptions of the optical properties of natural minerals⁽⁵²⁾ and synthetic minerals⁽⁴¹⁾ are also helpful, although they are not arranged primarily for immersion work. Other important reference works are listed in McVay's bibliography.⁽⁸⁶⁾

The petrographic microscope is a special type of microscope designed primarily for optical tests rather than for greater magnification and perfection of the image. The more important special features of a petrographic microscope are the polarizer (a calcite Nicol prism) for producing plane polarized light, the analyzer (another Nicol) whose vibration direction is normal to the polarizer and can be readily removed from the optical path, and the Amici-Bertrand lens set below the eyepiece and used in obtaining interference figures. It cannot be emphasized too

strongly that the "chemical" and "biological" microscopes fixed up with makeshift accessories are not suitable for crystallographic purposes. The usual cost of an ordinary petrographic microscope is about \$400 and varies considerably with the number of accessories, objectives, etc. Unlike X-ray equipment, much of the optical equipment has been well standardized, and the representatives of the companies listed below are well acquainted with the apparatus best suited for various types of problems. Moreover, their catalogues supply excellent technical information. These should be carefully read and it is also advisable to consult an experienced petrographer before placing an order. Companies manufacturing petrographic microscopes include

Bausch & Lomb Optical Company, Rochester, New York.
 E. Leitz, Inc., 730 Fifth Avenue, New York.
 Spencer Lens Company, Buffalo, New York.
 Carl Zeiss, Inc., 475 Fifth Avenue, New York.

Besides the microscope and its accessories, a series of immersion liquids are required varying in index of refraction by even steps. An ideal series of liquids can be prepared by mixing various proportions of two perfectly miscible end members of different refractive index. In such a series of liquids, the refractive index, dispersion, and temperature coefficient, $-dn/dt$, vary linearly with the composition.⁽⁴⁷⁾

Kaiser and Parrish⁽¹⁰⁶⁾ have recently described in detail the preparation of immersion liquids for the range $n_D = 1.411$ to 1.785, and their paper should be consulted for the details that cannot be given here. Since its publication, however, a far better low-index series has been found. Instead of *n*-decane and medium Government oil as suggested in the paper for the series 1.41 – 1.46, diethyl oxalate and dibutyl phthalate, $n_D = 1.409$ and 1.492 respectively, at 22°C. are recommended by Jewell J. Glass, U.S. Geological Survey. Univolt oil, $n_D = 1.475$, can be used in place of medium Government oil which apparently is no longer manufactured. For most work, it is advisable to have a set of about 75 bottles for the range 1.415 to 1.785 with a 0.005 index increment between adjacent bottles, *i.e.*, 1.600, 1.605, 1.610, . . . Increments smaller than 0.005 can be obtained by mixing drops from adjacent bottles on the microscope slide. Less than 1 per cent of the minerals listed by Larsen and Berman have a

β -index less than 1.400, and only 2 per cent have a β -index greater than 2.70. Fifty-four per cent of all minerals have a β -index between 1.475 and 1.700.

West^(79a) has prepared liquids of varying proportions of phosphorus, sulfur, and methylene iodide for the range $n_D = 1.78$ to 2.06, but they have a bad odor.

Thin sections are prepared commercially by the following for a nominal cost.

F. S. Reed & J. L. Mergner, 5519 Nevada Ave., N.W., Washington, D.C.
George S. Rev, Box 25, Room 108, Amsterdam Ave. at 119th St., New York.

W. Harold Tomlinson, 114 Yale Ave., Swarthmore, Pennsylvania.
Rudolf von Heune, 822 Dos Robles Place, Alhambra, California.

Other Means of Identification.—A number of other methods for identifying minerals are often found useful in conjunction with the X-ray method and the petrographic method. For example, in studying the clay minerals, the method of thermal analysis, described in Chap. V, is found particularly valuable for quantitative determinations of the minerals diaspore, gibbsite, and kaolinite in high alumina clays.

The true density of the mineral is an aid in identification. A convenient table listing minerals in order of their density is given by Rosenholtz and Smith,⁽⁴⁰⁾ Spencer,⁽¹⁹⁾ and Landes.⁽³⁴⁾ Although the density alone does not identify a mineral, it will place the mineral in a comparatively small group, which will greatly facilitate its further study by other means. Further work on pure, homogeneous minerals of known composition will give much more reliable data than now available.

The hardness of the mineral, also used as a means of identification but only in a rather general way, would be employed more as a confirmation of other data. Lists of minerals in order of their hardness are given by Rosenholtz and Smith⁽⁴⁰⁾ and also in various textbooks.

Fluorescence has been used in the last few years as a means of identifying certain types of minerals. For example, the dye morin will show little fluorescence when in contact with raw clay; but after heating to such a temperature that the clay structure is broken down, forming free alumina, then a typical fluorescence appears in the presence of morin. At higher temperatures where

alumina combines with the silica to form mullite and glass, the fluorescence subsides.

Color in itself is not usually a means of identification, because many of the minerals in the refractories are colored by traces of impurities such as iron, manganese, or chrome and the true mineral color is of little aid. However, a petrographer familiar with a particular type of refractory unconsciously uses the color of the minerals in thin sections as a guide in identification.

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kaolinite crystals,⁽⁷³⁾ gives an idea of what will be accomplished when we have had more experience with the electron microscope.

The clay particles have attached to their edges various adsorbed ions, such as Ca, Na or SO_3 , that markedly affect their physical properties. With the clay minerals is often associated organic matter such as lignite and humus, which may act as protective colloids and influence the physical properties of the clay. Most clays also contain impurities, often of large grain size, such as quartz, mica, feldspar, and other nonplastic minerals. Also the



FIG. 40.—Kaolinite crystals, 16,000 X. Taken with the electron microscope developed by the physics department of Massachusetts Institute of Technology.

clay minerals themselves can have iron and other metallic atoms in the crystal lattice.

The Origin of Clay.—Clay is always an altered product derived by weathering or hydrothermal action from rocks rich in feldspar. There is still no agreement among geologists as to the exact mechanism of clay formation or why various clay minerals are apparently obtained from the same parent rock. In most cases, the action is principally one of removal of the alkalis and decrease of the silica, the former being removed as soluble salts and the latter as colloidal silica. When silica removal is carried to the end point, as a result of the high permeability of the mass to the percolation of ground water, gibbsite or diaspore is the result. We are not sure whether a step-by-step process occurs or the reaction goes directly from the feldspar to an end point.

Clay minerals have been produced in the laboratory under certain conditions of temperature and acidity from feldspars, the reaction taking place most rapidly at about 300°C. It would have seemed curious a few years ago that under identical reaction conditions, the end product of potash feldspar, for example, is sericite whereas from calcium feldspar montmorillonite is produced; *i.e.*, the cation in the original rock, the original atomic arrangement, or both together seem to have some control over the type of end product. Geologists now are beginning to believe that in all metamorphic changes, there is some relation between the atomic structure of the original material and its product, as discussed more fully in Chap. IV.

Clays found in the same location as the parent rock from which they were formed are called "residual clays." Such clays usually contain rock fragments and thus require washing, for which reason they are not used to any great extent in refractories. The primary kaolins of North Carolina are a good example of a residual clay.

Transported clays are sediments deposited in lakes, swamps, or the ocean. They may be considerably altered during and after transportation. The sedimentary kaolins of Georgia and most fireclays are examples.

The classification of clays according to origin in Table 14, as suggested by Stout, will be helpful in understanding the process of clay formation.

The excellent chart by Chelikowsky,⁽²⁸⁾ shown in Table 15, gives a picture of geologic distribution of fireclays in the United States.

Clay Minerals.—The clay minerals may be divided into definite types; but since various degrees of isomorphism can occur, there is a variability in composition that makes classification and identification difficult. The grouping indicated in Table 16 gives a reasonable picture of their relationship based on our present knowledge. The atomic arrangement shown in Fig. 40*a* is a probable one, but only in the case of dickite is it universally accepted. In refractory clays, clay minerals are seldom found other than kaolinite, diaspore, and gibbsite.

The identification of the clay minerals, in many cases, is difficult because of their small size and indefinite composition. Petrographic methods can be used for the coarser grains. X rays

may be used to identify the finer fractions with a considerable degree of certainty, especially if specimens are prepared with a preferred orientation of the crystals. Another useful method is thermal analysis which can be made to give quantitative values, in some cases when the mineral is present in amounts as low as

TABLE 14.—CLASSIFICATION OF CLAYS AS TO ORIGIN*

Residual matter	No movement during formation	Products of ordinary weathering	From crystalline rocks	{ Impure residual clay Primary kaolin
			From sedimentary rocks	Impure residual clay Kaolinitic clay
		Same as above with additional chemical action	From crystalline rocks	Bauxite
			From sedimentary rocks	{ Bauxite Diaspore
Transported matter	Deposited in still water, little or no current action, seas, lakes, bogs, etc.		Products of ordinary weathering	{ Argillaceous shale Argillaceous silt
		Same as above with additional intensive chemical action	Sedimentary kaolin	Sedimentary kaolin
				Ball clay
	Deposited by slowly moving waters, streams, estuaries, etc.			Some bauxite
				Coal-formation clay
				Diaspore
Transported matter	Deposited by glacial action	Products of grinding with some weathering		{ Siliceous shale Siliceous silt
			Products of abrasion with slight weathering	Glacial clay or till
	Deposited by winds	Products of abrasion with slight weathering		Loess

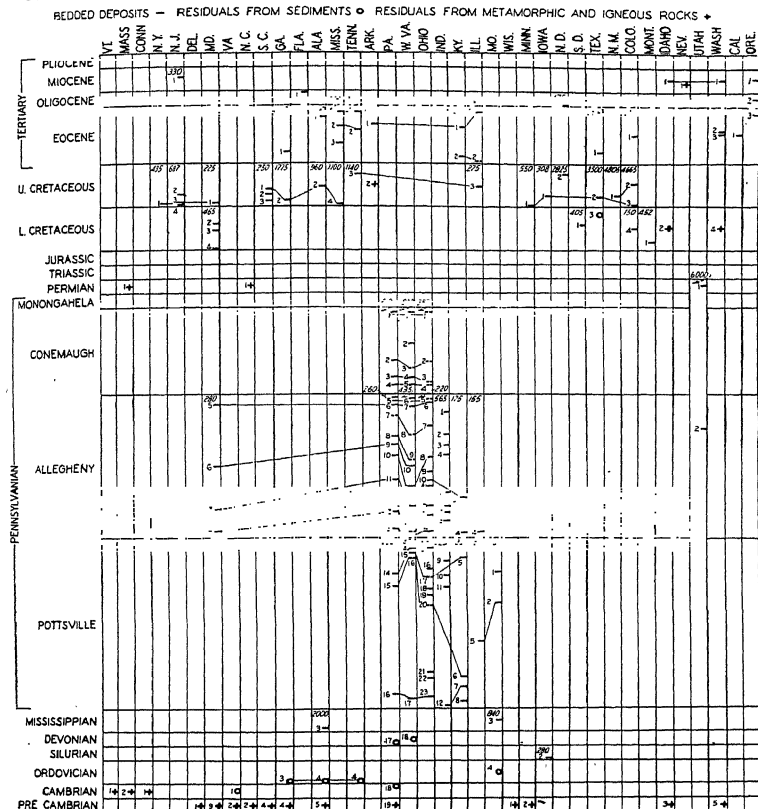
* Lecture on Clays by W. Stout, at Massachusetts Institute of Technology, 1937.

1 per cent by weight of the total. As the first two methods have been described in Chap. IV, only the method of thermal analysis will be discussed here.

If the clay mineral is placed in a furnace beside a neutral body, such as alumina, and heated at a uniform rate (12°C. per min.),

a temperature difference between the two that can be detected by a differential thermocouple will occur at different stages of the

TABLE 15.—FOR DETAILS CONCERNING NUMBERS REFER TO REFERENCE 28.*
GEOLOGIC DISTRIBUTION OF FIRE CLAYS IN THE UNITED STATES



* From J. R. Chelikowsky, J. Am. Ceram. Soc.

heating. The temperatures at which these differences occur are characteristic of the various clay minerals and serve as a means of identification even when they are mixed with others. A con-

TABLE 16.—THE CLAY MINERALS

Kaolinite group	Montmorillonite group	Micaeous group	Aluminous group
Kaolinite, $(\text{OH})_4\text{Al}_2[\text{Si}_2\text{O}_5]$ Dickite (same as kaolinite) Nacrite (same as kaolinite)	Pyrophyllite, $(\text{OH})_2\text{Al}_2[\text{Si}_2\text{O}_5]_2^*$ Talc, $(\text{OH})_2\text{Mg}_3[\text{Si}_2\text{O}_5]_2^*$ Montmorillonite, $(\text{OH})_2\text{Al}_2\text{--}$ $[\text{Si}_2\text{O}_5]_n\text{H}_2\text{O}^\dagger$ Nontronite, $(\text{OH})_2(\text{AlFe})[\text{Si}_2\text{O}_5]_2\text{--}$ $n\text{H}_2\text{O}^\S$ Beidellite (more Al than montmorillonite) Saponite, $(\text{OH})_2\text{Mg}_3[\text{Si}_2\text{O}_5]_{2n}\text{H}_2\text{O}$	Muscovite, $(\text{OH})_2\text{K}\cdot\text{Al}_3[\text{Si}_3\text{O}_{10}]^*$ Sericite (similar to muscovite) Hydromica (similar to muscovite) Illite $(\text{OH})_2\text{K}_x(\text{Al}_x\text{Fe}_4\text{Mg}_6)\text{--}$ $(\text{Si}_{9-x}\text{Al}_x)\text{O}_{20}$ Ordvician potash clays†	Gibbsite, $(\text{OH})_3\text{Al}^*$ Diaspore, $(\text{OH})\text{Al}^*$
Anauxite, $(\text{OH})_4\text{Al}_{2-n}[\text{Si}_{4+n}\text{O}_6]$ Halloysite (similar to kaolinite) Allophane (amorphous)			

* These minerals are not generally considered clay minerals by the geologist, but when finely ground behave like clays and are used as clays in ceramics.

† These clays may belong to the montmorillonite group.

‡ The Al may be partially or wholly replaced by Fe or Mg.

§ n is equal to zero for pyrophyllite and talc. It is variable for montmorillonite.







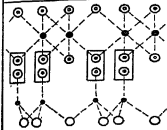
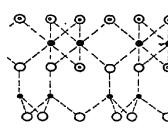
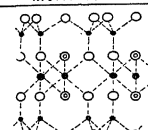
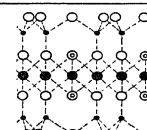
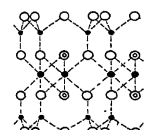
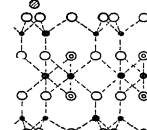

1-SILICON TETRAHEDRON  1 O -2 1 Si +4 3 O -6	2-ALUMINUM OCTAHEDRON  3 OH -3 1 Al +3 3 OH -3	3-MAGNESIUM OCTAHEDRON  3 OH -3 1 Mg +2 3 OH -3
4-HYDRATED SILICA  4 OH -4 4 Si +16 6 O -12	5-GIBBSITE  6 OH -6 4 Al +12 6 OH -6	6-BRUCITE  6 OH -6 6 Mg +12 6 OH -6
7-HALLOYSITE  6 OH -6 4 Al +12 6 OH -6 4 OH -4 4 Si +16 6 O -12	8-KAOLINITE  6 OH -6 4 Al +12 4 O -8 2 OH -2 4 Si +16 6 O -12	<ul style="list-style-type: none">• - Si• - Al● - Mg○ - O⊙ - OH
9-PYROPHYLLITE AND MONTMORILLONITE (IDEAL CASE)  6 O -12 4 Si +16 4 O + 2 OH -10 4 Al +12 4 O + 2 OH -10 4 Si +16 6 O -12	10-TALC  6 O -12 4 Si +16 4 O + 2 OH -10 6 Mg +12 4 O + 2 OH -10 4 Si +16 6 O -12	
11-NONTONITE  6 O -12 4 Si +16 4 O + 2 OH -10 4 Fe ⁺⁺⁺ +12 4 O + 2 OH -10 4 Si +16 6 O -12	12-MICA (ILLITE)  1 K +1 6 O -12 3 Si +1 Al +15 4 O + 2 OH -10 4 Al +12 4 O + 2 OH -10 3 Si +1 Al +15 6 O -12 1 K +1	
13-MONTMORILLONITE (SUBSTITUTED)  6 O -12 4 Si +16 4 O + 2 OH -10 3 Al +1 Mg +11 4 O + 2 OH -10 4 Si +16 6 O -12	<ul style="list-style-type: none">• - Si• - Al, Fe⁺⁺⁺● - Mg○ - O⊙ - OH⊙ - K	

Fig. 40a.—Structural data of the clay minerals. First column is schematic drawings (not to scale) of the atoms in a unit cell projected into one plane. Second column gives number and type of atoms in each lattice plane and third column gives the corresponding valence charges. Where (+) and (−) charges are equal, lattice is neutral; where unequal, the charge is equal to the algebraic difference. (From E. A. Hauser, *J. Am. Ceram. Soc.*)

venient apparatus is shown in Fig. 41 for this purpose. Figure 42 gives the differential temperatures for kaolinite, gibbsite, and diaspore plotted against the true temperature. The large endothermic peaks are caused by the energy required to expel the chemically combined water (the OH groups). The area under these peaks can be used as a quantitative measure of the amount

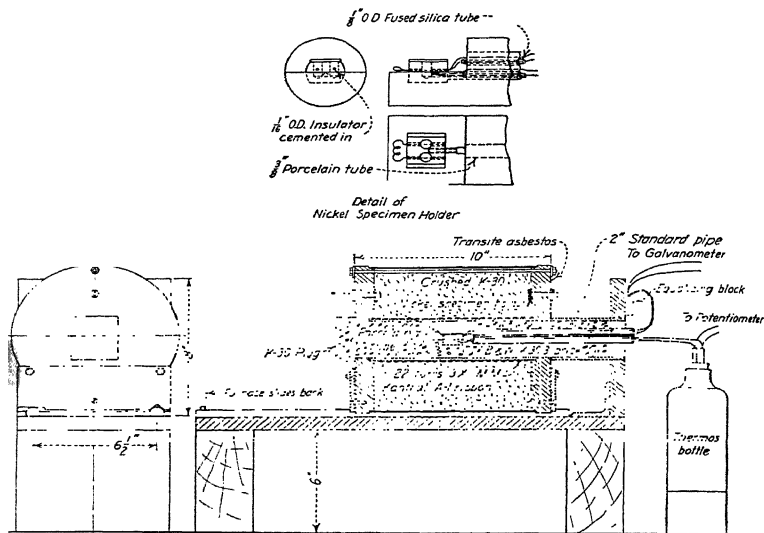


FIG. 41.—Differential thermal apparatus. (*J. Am. Ceram. Soc.*)

of that particular clay mineral. The areas for a 0.4-gr. sample are as follows:

Mineral	Area, °C. × seconds
Kaolinite.....	11,700
Diaspore.....	11,150
Gibbsite.....	21,800

As an example, consider the thermal curve for a Dutch Guiana clay in Fig. 42. It will be noted that the peaks corresponding to kaolinite and diaspore, which are of small magnitude, occur at the temperatures of the initial parts of their respective reactions and not at the maxima. The area of kaolinite reaction is 700, for the diaspore 700, and for the gibbsite 19,200. This represents

6 per cent kaolinite, 6 per cent diaspore, and 88 per cent gibbsite. Converting these to silica and alumina, 2.8 and 64.6 per cent is obtained respectively as compared with 4.5 and 58.4 per cent from a chemical analysis. If the 3.2 per cent Fe_2O_3 in the chemical analysis is counted as Al_2O_3 , the agreement is good.

The Exchangeable Bases.—Attached to the broken corners and edges of all clays are ions that are not really part of the crystal structure but are held in place by unsatisfied bonds and thus can be replaced by other ions. The finer the particle size of the clay

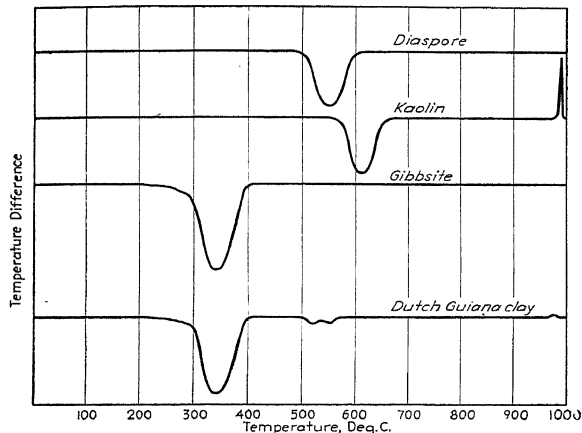


FIG. 42.—Thermal curves of clay minerals.

the more area is present for the attachment of these cations and the greater the so-called "base-exchange capacity," which is expressed in milliequivalents per 100 g. of dry clay. The exchange ions can be replaced by H^+ and OH^- on a clay by a number of methods, the most satisfactory being the treatment in a dialysis cell shown in Fig. 43. The clay slip, containing 5 per cent solids, is treated for about two weeks, the liquid in the end cells being replaced with distilled water at frequent intervals until a constant value of current is reached. Even with this long treatment there is reason to believe that many adsorbed ions or groups cannot be entirely removed. To produce a really clean clay calls for a more elaborate procedure. The liquid from the end cell may be evaporated and analyzed for the elements

extracted. The exchangeable metallic bases reported by Graham and Sullivan⁽⁵³⁾ for several clays are shown below.

Clay	Exchangeable metallic bases				
	Ca	Mg	Na	K	Total
Georgia kaolin.....	0.4	0.6	0.1	Trace	1.1
Pennsylvania flint clay.....	2.5	1.8	0.5	0.4	5.2
Kentucky flint clay.....	3.4	2.0	0.9	0.8	7.1
Kentucky ball clay.....	7.1	3.8	0.5	0.4	11.8

The total base-exchange capacity is believed in general to be as follows:

	Milliequivalents/100 g.
Kaolin.....	2-6
Ball clay.....	10-20
Bentonite.....	50-100

After a hydrogen clay is produced by dialysis, ions in any amount up to the saturation point can replace the hydrogen and

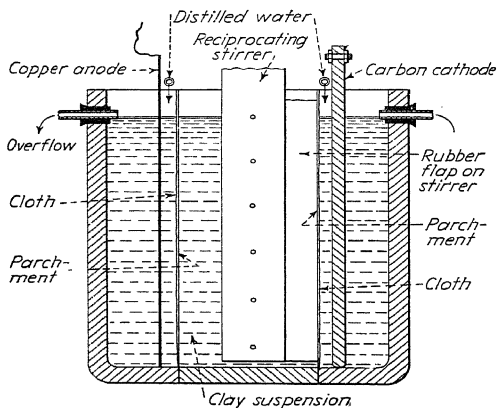


FIG. 43.—Three-compartment dialysis cell.

hydroxyl group to give a clay with controlled adsorbed ions. The type of ion present in the clay profoundly influences its physical

properties, producing a variable that has not generally been taken into account in the past. Just one example will bring this out for a fine-grained kaolin.

Milliequivalents of Na ⁺ per 100 g. of Clay	Dry Strength Modulus of Rupture, lb. per sq. in.
0 (hydrogen clay)	430
7	700
14	1,000

The control of exchangeable bases is particularly important when using clays in casting slips.

Organic Matter.—Many clays contain appreciable amounts of organic matter, such as lignite or humic acid. Dark ball clays and less pure bog clays contain especially large amounts. Although little scientific work has been carried out to determine the influence of this matter on the properties of the clay, it is generally agreed that it does influence the plasticity, dry strength, and slip-forming properties, either because of an organic colloid or because of the organic acid. This is an important field for research; the ceramist and the soil chemist should cooperate more closely along these lines in the future. Nearly all organic matter can be removed by long digestion with 30 per cent hydrogen peroxide.

The ageing of clays, although little practiced in the refractories industry, is connected to some extent with bacterial action in the clay mass which produces substances acting much like the organic acids.

Accessory Minerals.—All clays contain mineral fragments of a nonclay type which have an important influence on the properties of the clay. The minerals commonly found are as follows:

Quartz

Feldspars (orthoclase, plagioclase)

Micas (muscovite and biotite)

Iron Minerals (hematite, magnetite, limonite, pyrite, siderite)

Titanium Minerals (rutile, anatase)

Limestone (calcite, dolomite)

Magnesite

Gypsum

Garnet

Tourmaline

A few of these minerals, such as quartz, act as a refractory nonplastic, whereas the others act more or less as fluxes and reduce the refractoriness of the clay.

Physical Properties.—Only within the last few years has it been possible to measure the full range of particle sizes in clays with assurance. The size distributions for a few typical clays

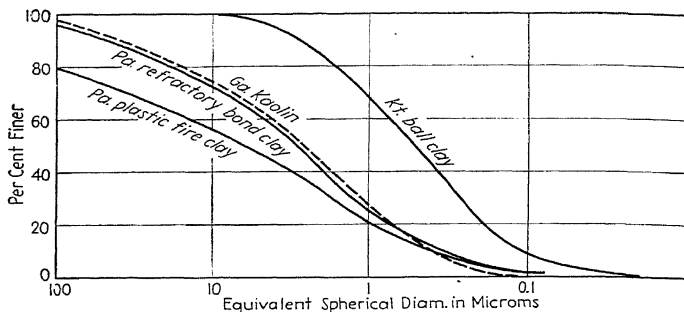


Fig. 44.—Particle size distribution for various clays.

are shown in Fig. 44. It will be noticed, first, that there are few particles below 0.1μ but a large portion are below 1μ , giving the greatest frequency between 0.2 and 0.8μ . As the surface area increases enormously with even a slight increase in the proportions of fines, careful measurements are needed in this range. It will be noted that the plastic fireclays, though coarser than the kaolin in the larger size range, have more very fine particles, which accounts for their relatively greater plasticity.

In order to study the influence of grain size on the physical properties, it is most convenient to split a clay up into a number of nearly monodisperse fractions for which the mean size can be accurately determined. It will be found that most of the physical properties vary with the particle size, as shown by Whittaker^(55a) in Table 17 for a clay containing wholly kaolinite.

The plasticity, or workability, varies greatly among clays. In general, the finer grained clays, free from nonplastics, are most plastic. The plasticity of most clays can be increased by fine grinding, ageing, adding organic matter, or mixing in another clay of fine-grain size, such as bentonite.

Whereas some clays readily slake in water, others will remain under water indefinitely without breaking down. The flint clays and shales consolidated by chemical action cannot be broken down without considerable grinding, but a plastic fireclay will quickly disperse into its ultimate particles when added to water. Undoubtedly the adsorbed ions have an important influence on the slaking. For example, a hard and a soft kaolin of the same chemical composition, both containing wholly kaolinite, show, in the first case, ten times as much exchangeable calcium ions as in the latter.

TABLE 17.—VARIATION OF PHYSICAL PROPERTIES WITH PARTICLE SIZE

Mean diameter, microns	Surface area per 100 g., sq. cm.	Drying shrinkage, per cent	Dry strength, lb. per sq. in.	Relative plasticity
8.50	13×10^4	0.0	4.6	None
2.20	392	0.0	14.0	None
1.10	794	0.6	64.0	4,400
0.55	1,750	7.8	47.0	6,300
0.45	2,710	10.0	130.0	7,600
0.28	3,880	23.0	458.0	8,200
0.14	7,100	30.5	296.0	10,200

In general, the fine-grained plastic clays have a high shrinkage, because they have large numbers per unit distance of interparticle water films, whose elimination causes the shrinkage. Montmorillonite, the mineral in bentonite, increases in the distance between the atomic planes of a single crystal by water molecules entering the crystal structure. This is the reason for the great swelling power of some bentonites.

The finer grained clays generally have high dry strengths, but other factors such as adsorbed ions and organic matter are important. As yet, we have little explanation of the forces holding the particles together in a dry clay. This is a field for interesting research.

The color of clay is of no great importance in refractories manufacture, except as an indication of impurities.

Kaolin $(\text{OH})_4\text{Al}_2(\text{Si}_2\text{O}_5)$.—Pure kaolin has a fusion point of 1785°C . (3245°F .), although this may drop a few degrees if any impurities are present. The residual or true kaolin occurs in many

localities in rather small deposits in the southeastern United States. There are also a few deposits in Vermont and Massachusetts. The most workable deposits are the sedimentary or plastic kaolins, which are rather widely distributed in this country in the southeastern states where the beds are of great extent, averaging from about 15 to 30 ft. in thickness with about the same thickness of overburden. The kaolin is usually mined by stripping off the overburden and taking out the clay by hand or with a power shovel. There are considerable deposits of kaolin in England, which are mined as English china clay. Excellent deposits also occur in Czechoslovakia and Germany. Typical analyses of some kaolins are given in Table 18, and deposits are shown on the maps of Figs. 45 and 47.

TABLE 18.—ANALYSES OF TYPICAL KAOLINS

Constituent	Georgia kaolin per cent ^(212a)	English china clay (washed), per cent	Vermont residual kaolin, per cent ⁽²²⁾	North Carolina kaolin (washed), per cent
Silica, SiO ₂	45.8	48.3	58.0	45.8
Alumina, Al ₂ O ₃	38.5	37.6	26.9	36.5
Titanium oxide, TiO ₂	1.4		1.4	0.0
Ferric oxide, Fe ₂ O ₃	0.7	0.5	1.5	1.4
Calcium oxide, CaO.....	Trace	0.1	0.4	0.5
Magnesium oxide, MgO.....	Trace		0.9	
Alkalies.....		1.6	2.2	0.3
Combined water.....	13.6	12.0		13.4
Total.....	100.0	100.1	100.2	97.9

Clays and Minerals Related to Kaolin.—There are a number of hydrated aluminum silicates of the kaolin group, most of which are rare.

Halloysite, (OH)₄Al₂(Si₂O₅), occurs as a fine-grained, soapy white clay. This mineral has often been confused with fine-grained kaolinite but can be distinguished by its thermal curve.⁽⁷⁵⁾ A typical analysis is shown in Table 19.

Allophane, or indianait, is a waxy white clay found in Indiana and Kentucky with the composition shown in Table 19. It is so fine grained as to be amorphous.

Several other members of the kaolinite group of rare occurrence are mentioned in the tables at the end of the chapter.

TABLE 19.—ANALYSES OF MINERALS RELATED TO KAOLINITE

Constituent	North Carolina halloysite, per cent	Allophane I, per cent ^(212a)	Allophane II, per cent ^(212a)
Silica, SiO ₂	44.3	43.3	32.
Alumina, Al ₂ O ₃	37.4	39.9	46.
Ferric oxide, Fe ₂ O ₃ ..	0.4		0.
Lime, CaO.....	0.2	0.7	0.
Magnesia, MgO.....	0.1		0.5
Alkalies.....	0.2	0.6	
Water of constitution	15.1	15.5	19.4
Total.....	97.7	100.0	100.0

TABLE 20.—ANALYSES OF BALL CLAYS

Constituent	Mayfield, Ky., per cent ^(212a)	Tennessee, per cent
Silica, SiO ₂	56.4	46.9
Alumina, Al ₂ O ₃	30.0	33.2
Ferric oxide, Fe ₂ O ₃ ..		2.1
Lime, CaO.....	0.4 }	
Magnesia, MgO.....	Trace }	0.8
Potash, K ₂ O.....	3.3 }	
Soda, Na ₂ O.....	2.0 }	0.7
Titanium oxide, TiO		.
Water (combined)...	7.9	16.5
Total.....	100.0	100.2

Ball Clays.—Ball clays are distinguished by their fine grain, lignite content, and high plasticity but are not usually so refractory as kaolins, the fusion point being around 1675°C. (3050°F.). They are sometimes used in refractories as a bond for harder and less plastic clays, but their greatest use is in whiteware. The analyses of two typical ball clays are given in Table 20. They are found almost exclusively in Kentucky and Tennessee as shown in Fig. 45.

Fireclays.—The so-called “fireclays” include nearly all clays that have a fusion point above approximately 1600°C. (2912°F.)

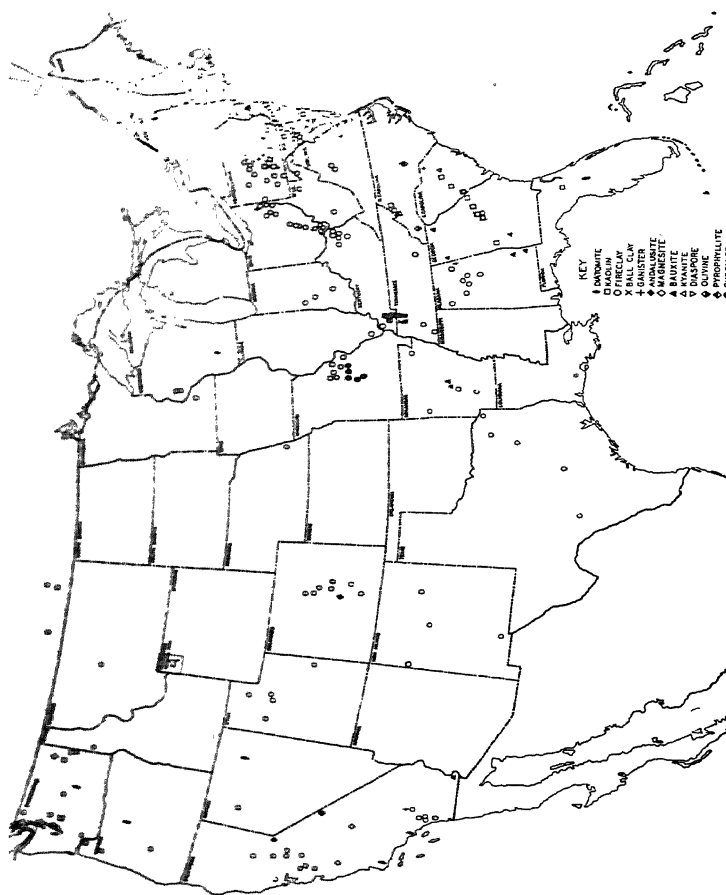


FIG. 45.—Working deposits of refractory materials in the United States.
Inc., New York, No. 10,074).

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and are not white burning. Fireclays are widely distributed and vary greatly in their characteristics. They may be roughly divided into the following types: flint clays, which (owing to great pressure encountered since they were deposited) are compressed into a hard, rocklike mass and require fine grinding to develop plasticity; plastic clays, which are soft and easily tempered into a plastic mass; and refractory shales, which can usually be made directly into brick without the addition of bonding clay.

TABLE 21.—ANALYSES OF FIRECLAYS
(Analyses by Downs Shaaf^(42a))

	Plastic, Law- rence, Ohio	Flint, Cam- bria, Pa.	Flint, Carter, Ky.	Semi- flint, Jackson, Ohio	Semi- flint, Clear- field, Pa.	Plastic, Vinton, Ohio	Flint, Mont- gomery, Mo.
SiO ₂	58.10	44.43	44.78	50.32	43.04	46.72	44.04
Al ₂ O ₃	23.11	37.10	35.11	31.53	36.49	33.06	38.03
Fe ₂ O ₃	1.73	0.46	1.18	1.02	1.37	0.68	0.63
FeO	0.68	0.55	0.74	0.35	0.83	0.55	0.22
FeS ₂	0.55	0.22	0.14	0.12	0.24	0.34	0.01
MgO	1.01	0.19	0.55	0.18	0.54	0.19	0.12
CaO	0.79	0.60	0.77	0.80	0.74	0.61	0.40
Na ₂ O	0.34	0.10	0.29	0.07	0.46	0.42	0.10
K ₂ O	1.90	0.55	0.44	0.05	1.10	1.53	0.22
H ₂ O—	2.27	0.80	0.84	2.47	0.82	2.21	0.78
H ₂ O+	7.95	12.95	13.07	11.25	12.44	11.50	13.55
CO ₂	0.05	0.11	0.07	0.14	0.05	0.02	0.04
TiO ₂	1.40	1.84	2.22	1.45	1.79	2.20	1.82
P ₂ O ₅	0.17	0.21	0.02	0.48	0.10	0.12	0.28
SO ₃	0.03	0.01	0.01	0.01	0.01	0.01	0.01
MnO	0.01	0.01	0.02	0.02	0.01	0.01	0.01
ZrO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Org. C	0.22	0.10	0.11	0.07	0.22	0.04	0.01
Org. H	0.03				0.03		

Analyses of a number of types of fireclays are given in Table 21, and the distribution in the United States on the map of Fig. 45.

Super-duty fireclay brick are usually made from pure Missouri flint clays with approximately the composition in Table 21. They have a low porosity and show little or no reheat shrinkage.

2. Clays and Minerals High in Alumina: Hydrated Alumina. Some of the most important refractory materials are those containing the mineral diaspore, usually occurring with kaolinite in

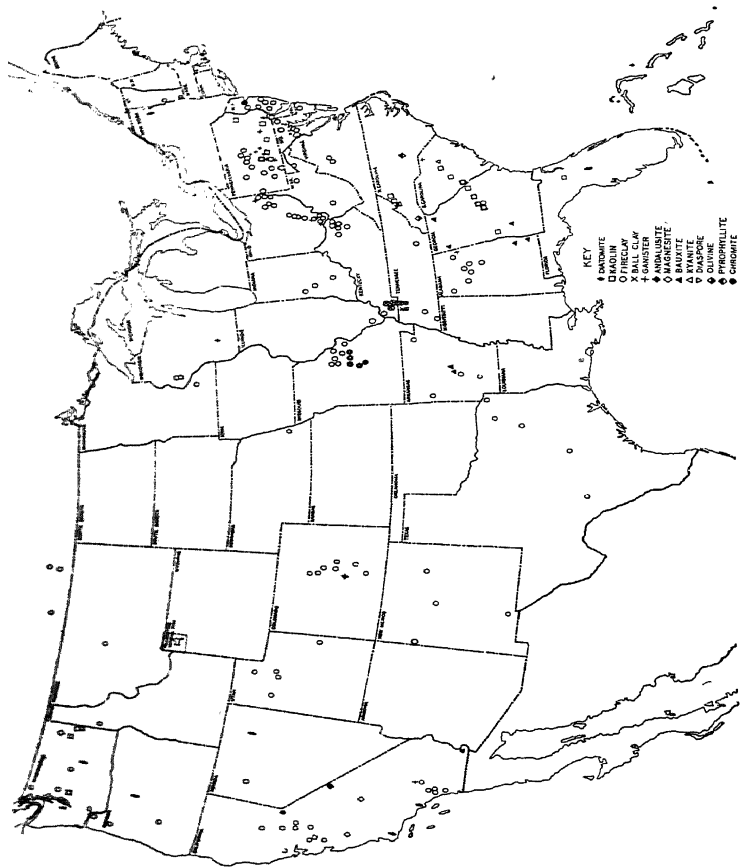


FIG. 45.—Working deposits of refractory materials in the United States.
Inc., New York, No. 10,074.

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and are not white burning. Fireclays are widely distributed and vary greatly in their characteristics. They may be roughly divided into the following types: flint clays, which (owing to great pressure encountered since they were deposited) are compressed into a hard, rocklike mass and require fine grinding to develop plasticity; plastic clays, which are soft and easily tempered into a plastic mass; and refractory shales, which can usually be made directly into brick without the addition of bonding clay.

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SiO ₂	58.10	44.43	44.78	50.32	43.04	46.72	44.04
Al ₂ O ₃	23.11	37.10	35.11	31.53	36.49	33.06	38.03
Fe ₂ O ₃	1.73	0.46	1.18	1.02	1.37	0.68	0.63
FeO	0.68	0.55	0.74	0.35	0.83	0.55	0.22
FeS ₂	0.55	0.22	0.14	0.12	0.24	0.34	0.01
MgO	1.01	0.19	0.55	0.18	0.54	0.19	0.12
CaO	0.79	0.60	0.77	0.80	0.74	0.61	0.40
Na ₂ O	0.34	0.10	0.29	0.07	0.46	0.42	0.10
K ₂ O	1.90	0.55	0.44	0.05	1.10	1.53	0.22
H ₂ O—	2.27	0.80	0.84	2.47	0.82	2.21	0.78
H ₂ O+	7.95	12.95	13.07	11.25	12.44	11.50	13.55
CO ₂	0.05	0.11	0.07	0.14	0.05	0.02	0.04
TiO ₂	1.40	1.84	2.22	1.45	1.79	2.20	1.82
P ₂ O ₅	0.17	0.21	0.02	0.48	0.10	0.12	0.28
SO ₃	0.03	0.01	0.01	0.01	0.01	0.01	0.01
MnO	0.01	0.01	0.02	0.02	0.01	0.01	0.01
ZrO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Org. C	0.22	0.10	0.11	0.07	0.22	0.04	0.01
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2. Clays and Minerals High in Alumina: Hydrated Alumina. Some of the most important refractory materials are those containing the mineral diaspor, usually occurring with kaolinite in

rying proportions. The clays vary from nearly pure diaspore to mixtures containing nearly all kaolinite. Most of them occur in Missouri, although there are a few other minor locations. From these clays are made the high alumina brick having alumina contents of 50, 60, 70, and 80 per cent according to the classification. They may also have some corundum added.



Fig. 46. A gibbsite nodule cut in half about one-fourth natural size.

There are other high-alumina clays containing gibbsite or mixtures of gibbsite and kaolinite. The purer materials, such as those from Dutch

Guiana (Fig. 46), contain almost all gibbsite, but the aluminous ones from the South have more or less kaolinite mixed with them.

TABLE 22.—HIGH-ALUMINA CLAYS

Clay	Dutch Guiana gibbsite	First- grade diaspore, Mo.	Bauxite, Ga.	Burley, Flint, Mo.	Second- grade diaspore, Mo.
Chemical Analyses					
Silica	4.5	10.9	26.0	33.8	29.2
Alumina	58.4	72.4	54.0	49.4	53.3
Titanium oxide	2.9	3.2	2.1	2.6	2.7
Iron oxide	3.2	1.1	1.0	1.8	1.9
Lime	0.4				
Magnesia					
Alkalies					
Combined water	30.6	13.5	16.1	12.0	12.0
Total	100.0	101.1	99.2	99.6	99.1
Thermal Analyses					
Kaolinite	6	None	67	71	18
Diaspore	6	90	None	26	53
Gibbsite	88	None	38	None	None

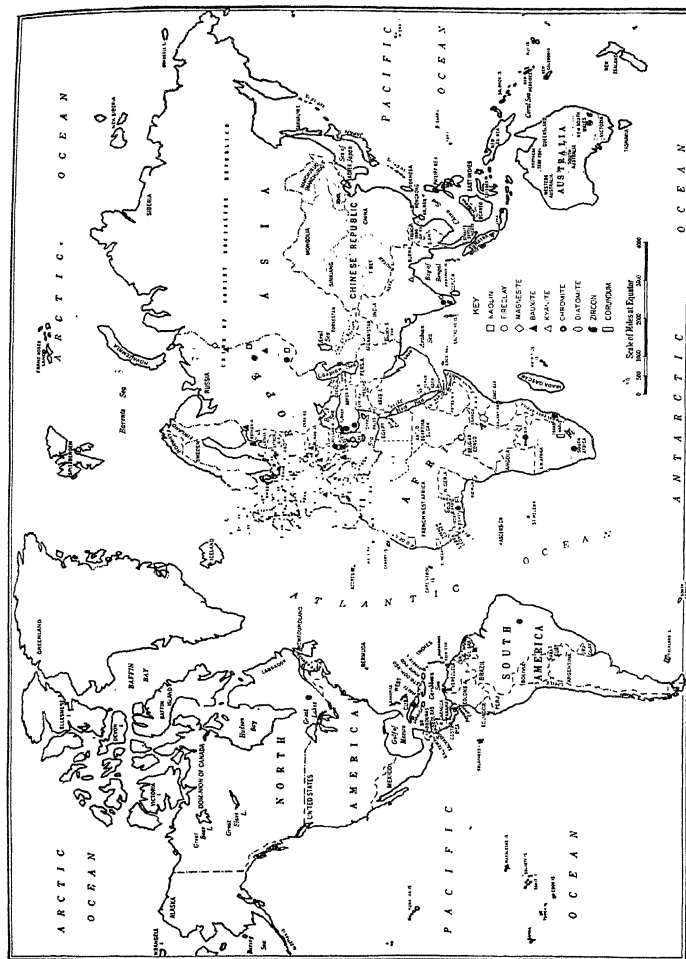


Fig. 47.—Important deposits of refractory materials in the world. (Copyright, American Map Company, Inc., New York, No. 10,074.)

The term "bauxite" is used here for clays containing a mixture mainly of kaolinite and gibbsite. The bauxitic clays have not been used for refractories to any extent because of their less favorable shrinkage properties.

The locations of the principal deposits of high-alumina clays are shown in Figs. 45 and 47. Both the chemical and mineral



FIG. 48.—Thin section of sillimanite. (250X)

analyses of some typical high-alumina clays are shown in Table 22. The thermal method is particularly valuable in studying these clays because it readily distinguishes between diaspore and gibbsite.

Sillimanite. Types of Minerals.—There are a number of minerals having a composition $\text{SiO}_2\text{-Al}_2\text{O}_3$, which gives a silica content of 37 per cent and an alumina content of 63 per cent. Sillimanite occurs in a number of small deposits in this country, but the largest source of supply is in India. Andalusite has a different

crystal form from sillimanite and is found in small deposits in California and in considerable quantities in Spain. Kyanite occurs in Switzerland, in some of the Southern states, and on the West Coast of the United States. All these minerals are decomposed to mullite and silica on heating above 1555°C. (2831°F.)

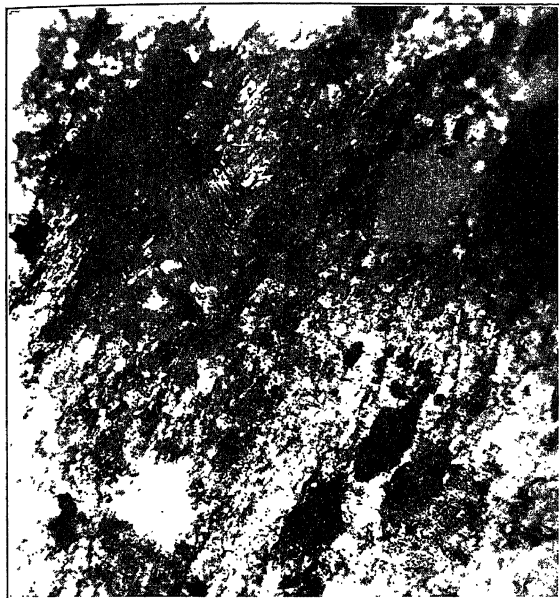


FIG. 49.—Thin section of andalusite; 250 X, with crossed Nicol prisms and gypsum plate.

when pure and at a lower temperature when fluxes are present. These materials are being used to a considerable extent as refractories at the present time. The great problem is to concentrate the ore efficiently and at the same time provide fairly coarse grains. Thin sections of these minerals are shown in Figs. 48 to 50.

Topaz.—This mineral has been found in India in some quantity, but recently an important deposit has been discovered in South Carolina.^(132a) Topaz has the composition $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ and

thus will readily transform to mullite on firing, hence offering attractive possibilities as a raw material.

Pyrophyllite.—This talclike mineral is found in a number of deposits in the South and has been used in some refractories in



FIG. 50.—Thin section of kyanite ore. The large crystal on the left border is kyanite which shows pronounced cleavage and numerous inclusions. The rest of the field shows a grain of staurolite, three smaller garnet crystals with muscovite, biotite, quartz, feldspar, and magnetite; 40 \times , with ordinary transmitted light.

place of clay. Its formula of $(\text{OH})_2\text{Al}_2(\text{Si}_2\text{O}_5)_2$ does not give so high an alumina content as kaolin. However, it has been successful in some cements and plastics.⁽¹²⁸⁾

Forms of Alumina.—Alumina occurs in a number of forms. The α -alumina is identical with the natural mineral corundum, which is a trigonal crystal with a specific gravity of 4.0. This mineral apparently is very stable and is almost always produced from cooling fusions. γ -alumina is hexagonal but has a spinellike

structure and a specific gravity of 3.31 and is generally formed by the heating of hydrous alumina materials such as kaolin or gibbsite. At higher temperatures, it slowly inverts to the α -form. An isometric form of alumina has been described having a specific gravity of 3.47 and is found in some quickly cooled



Fig. 51.—Thin section showing appearance of corundum crystals formed in the electric furnace; 80 X, with crossed Nicol prisms.

melts. Apparently this form is not found to any extent in refractories.

The so-called " β -alumina" has been found by Beevers and Ross to be not a form of alumina but a compound consisting of 11 molecules of Al_2O_3 and 1 molecule of soda or potash. A " ζ -alumina" has been described as occurring only in melts containing lithium. Probably this is similar to the β -alumina, being a compound of lithium oxide and alumina.

Corundum.—Corundum, or emery, Al_2O_3 , is found in many small deposits, the most important being in Asia Minor, South

Africa, Greece, Ontario, and North Carolina. It has not been used to any extent for a refractory but would seem to be a material worth more investigation. A thin section of artificial corundum is shown in Fig. 51. Crystalline alumina made in electric furnaces is used to a considerable extent as a refractory.

3. Silica Minerals. *Ganister.*—The most commonly used silica mineral for refractories is ganister, a common name for true quartzite. Not all quartzites are suitable for making refractories, as they must be of high purity and have good mechanical strength. The principal deposits of ganister in this country are the Medina sandstone of Pennsylvania; the Baraboo quartzite of the Devil's Lake region, Wisconsin; and the quartzites of Alabama and Colorado. A quartzite is usually mined from the bodies of talus or slide rock occurring on the mountain slopes. A few typical analyses of quartzites are given in the following table, and a thin section is shown in Fig. 52.

TABLE 23.—ANALYSES OF QUARTZITES

Constituent	Medina quartzite, per cent ⁽¹⁴¹⁾	Baraboo quartzite, per cent ⁽¹⁴¹⁾	Alabama quartzite, per cent ⁽¹⁴¹⁾	Sharon conglomer- ate ^(153a)
Silica, SiO ₂	97.8	98.2	97.7	98.0
Alumina, Al ₂ O ₃	0.9	1.1	1.0	0.9
Ferric oxide, Fe ₂ O ₃	0.9	0.2	0.8	0.9
Lime, CaO.....	0.1	0.0	0.1	0.3
Magnesia, MgO.....	0.2	Trace	0.3	Trace
Alkalies, K ₂ O, Na ₂ O.....	0.4	0.1	0.3	0.2
Total.....	100.3	99.5	100.2	100.3

The fusion point of quartzite^(153a) is very close to 1700°C. (3090°F.); and, like mullite, it shows little softening below its melting point. This is its chief value when used as a refractory, as it retains its resistance to load at higher temperatures than fireclay materials. Owing, however, to their high thermal expansion, silica materials are very sensitive to temperature changes in the low-temperature ranges. Most silica refractories are made in the form of bricks or special shapes, but some ganister is used in rammed furnace bottoms.



FIG. 52.—Thin section of quartzite. The light and dark areas in this photomicrograph show quartz grains at different orientation with respect to the plane of polarization of the Nicol prisms; 80 \times , with crossed Nicol prisms.

TABLE 24.—ANALYSES OF DIATOMACEOUS EARTHS

Constituent	Oberhole, Germany, per cent	California, per cent
Silica (SiO_2).....	87.9	85.3
Alumina (Al_2O_3).....	0.1	5.4
Ferric oxide (Fe_2O_3).....	0.7	1.1
Calcium carbonate (CaCO_3).....	0.7	1.1
Organic matter.....	2.3	
Water.....	8.4	5.6
Total.....	100.1	98.5

Firestone.—Natural stone refractories are still used to some extent. They consist of an easily cut sandstone^(156,157,158) or a mica schist. In either case, the stone must have a certain flexibility of structure to reduce the tendency to spall. Firestone is rather wide in occurrence, working deposits being found in Pennsylvania, Tennessee, Ohio, and several other states.

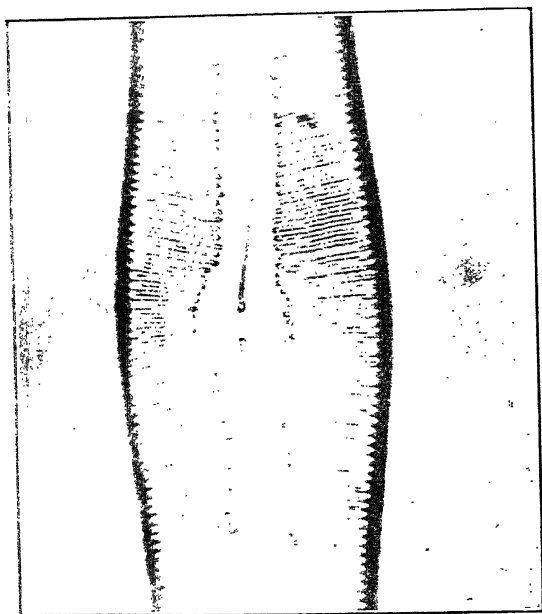


FIG. 53.—Photomicrograph of a single diatom showing fine cell structure. This structure is the reason for the excellent heat insulating properties which diatomaceous earth possesses; 800 X, with ordinary transmitted light.

Sand.—A small amount of beach sand is used for furnace bottoms, as, for example, in the hearth of malleable-iron melting furnaces, but the volume used is very small compared with the refractories made from quartzite.

Diatomaceous Earth.—Another type of siliceous mineral, used mainly as a heat insulator, is diatomaceous earth (infusorial earth or kieselguhr), a widely distributed material. It is com-

posed of the skeletons of diatoms, which are microscopic organisms (Fig. 53). The desirable characteristics of this material are its closed cells and high porosity, which gives a low density and a low thermal conductivity. Analyses of two typical samples of infusorial earth are given in Table 24.

4. Magnesite and Lime.—Magnesite refractories are of great importance in the metallurgy of steel and nonferrous metals, as they are used almost exclusively for the part of the furnace that comes in contact with the molten metal and slag, a large volume being used in the bottoms of the basic open-hearth furnaces in the form of lumps and brick.

Magnesite.—Magnesite occurs in nature as the carbonate; and two types have generally been recognized, the crystalline and the dense, the latter usually being of greater purity. The crystalline material is found in considerable quantity in Austria, Russia, Manchukuo, Quebec, and the state of Washington. Figures 45 and 47 show the important deposits. The Austrian material usually runs rather high in iron and has been in great demand for metallurgical work because it will frit together into a solid mass at available temperatures. The magnesite from Quebec runs higher in lime. The Washington magnesite occurs in large quantities and is relatively pure.

TABLE 25

Constituent	Austrian	Austrian	Manchu- kuo	Washing- ton	Greece	California sea water
SiO ₂	5.8	1.0	3.7	4.9	6.6	5.1
Al ₂ O ₃	1.7	1.0	1.0	1.5	4.4	0.5
Fe ₂ O ₃	4.0	6.9	1.5	3.4		0.2
CaO	5.0	2.1	1.6	2.8	2.4	1.8
MgO	83.0	88.6	92.0	87.1	86.4	91.7
Ignition loss	0.2	0.3	0.1	0.1	0.2	0.3
Total	99.7	99.9	99.9	99.8	100.0	99.6

The dense type of magnesite usually occurs in veins and lenses, the most important deposits being found on the island of Euboea off the coast of Greece. The purity of this deposit, if carefully selected, is high, running between 94 and 98 per cent magnesium carbonate. Several California deposits have been operating for

a number of years and give a pure material. Magnesite from sea water in California is now assuming importance.

Several analyses of burned magnesite are given in Table 25, and a thin section is shown in Fig. 54.

Magnesite is produced as caustic-burned and dead-burned material. The latter is used for refractories and is fired at 1550

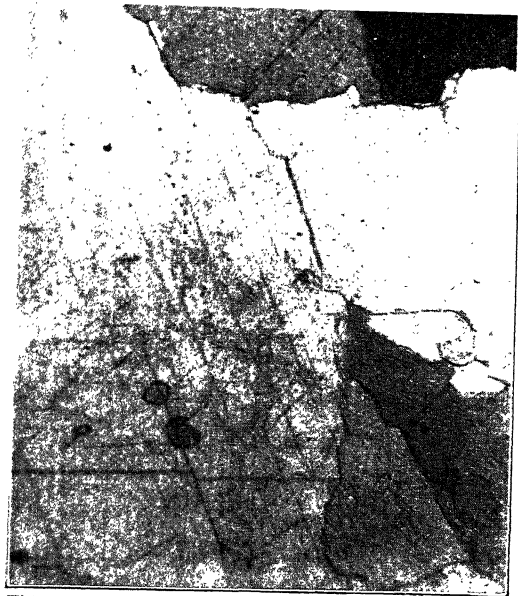


FIG. 54.—Thin section of crystalline magnesite. This section shows the high relief and cleavage which this mineral possesses; 80 X, with crossed Nicol

to 1750°C. (2820 to 3180°F.) to drive off practically all the CO₂ and form crystals of periclase. Magnesite can be fused in the electric furnace and, on cooling slowly, forms relatively large periclase crystals.

Dolomite.—Dolomite is a solid solution of calcium and magnesium carbonate and, when pure, has an equal number of molecules of both, although all ratios occur in nature. Dolomites are very

widely distributed. They have been used to some extent to replace magnesite in open-hearth bottoms but, because of their slaking properties, are not so good as magnesite. Although many experiments have been made on the production of a success-



FIG. 55.—This photomicrograph is a thin section of chromite with some serpentine associated with it. The chromite is the darker-colored areas, which show very irregular cleavage. Chromite is nearly opaque, and the thin section must be very thin to render it transparent; 250 diameters and wave plate to give second order green, and photographed through a "B" Wratten filter (deep red).

ful dolomite brick, as yet all the difficulties have not been overcome.

Lime.—Lime, next to magnesite, is believed to be the most refractory commercial oxide and is very widely distributed in deposits of great purity. However, little success has been had with this material as a refractory, for it slakes readily in both air and water. However, if lime is heated to 1800°C. (3270°F.)

in an oxidizing atmosphere, it may be crystallized and in this form has a considerable resistance to slaking.

Olivine, Mg_2SiO_4 .—This magnesium silicate usually has 5 to 8 per cent of the MgO replaced by FeO in the theoretical formula. By mixing with the correct amount of magnesite, this material has been used in the last few years to make forsterite refractories. Olivine deposits are widespread, but excellent material occurs in the dunite rock of North Carolina.

5. Chromite.—The principal mineral in commercial chrome ore is chromite, with the formula Cr_2FeO_4 . When pure, it contains 32 per cent iron oxide and 68 per cent chromic oxide, but the commercial ores contain at best only 50 per cent chromic oxide and often run as low as 30 per cent. This mineral is a spinel, and part of the iron and chromic oxide are replaced by either magnesia or alumina; accordingly the ore may vary quite widely in analysis and yet maintain its refractory properties. The ore cannot always be cheaply concentrated; but, as it ordinarily has a fusion point above $1930^{\circ}C.$ ($3510^{\circ}F.$), the raw ore is usually satisfactory. Great improvements have been made in some ore by adding magnesia, which combines with the silica to form forsterite.^{151a} A thin section of chromite is shown in Fig. 55.

TABLE 26

Constituent	Turkey	Rhodesia	Philippines	New Caledonia	Russia	Cuba
Cr_2O_3	46.6	45.4	32.1	54.5	46.2	30.5
SiO_2	6.7	7.5	5.3	3.1	4.0	6.1
Al_2O_3	12.5	13.8	27.6	11.0	14.6	27.5
FeO	12.9	15.1	13.0	19.5	15.6	14.2
CaO	1.2	0.5	1.1	1.5	0.3	0.9
MgO	17.3	13.6	18.2	8.0	15.4	18.3
Total	97.2	95.9	97.3	97.6	96.1	97.5

The largest supplies of chrome ore come from Rhodesia and New Caledonia. There are, however, considerable deposits in Turkey, Cuba, the Philippines, Russia, and Greece and small deposits in Canada, California, Oregon, and Alaska. The analyses of several chrome ores are given in Table 26.

6. Less Common Refractory Oxides. Zirconia.—The most available minerals for refractories belonging to this class are zirconite and baddeleyite, with the formula ZrO_2 . They are found in deposits of considerable extent in Brazil and also Ceylon, with some other closely allied zirconium minerals. The amount of zirconia present is between 60 and 80 per cent. Pure, electrically fused zirconia has a constant volume and is capable of withstanding very high temperatures. An analysis of a Brazilian baddeleyite is given below.

TABLE 27.—ANALYSES OF ZIRCONIUM MINERALS

Constituent	Baddeleyite, per cent	Zircon, per cent
Ferric oxide, Fe_2O_3	1.6	0.1
Alumina, Al_2O_3	7.8	1.4
Lime, CaO	0.0	
Silica, SiO_2	27.3	40.4
Zirconium oxide, ZrO_2 ..	60.4	51.6
Undetermined.....	2.9	6.5
Total.....	100.0	100.0

Zircon.—Zircon, with the formula ZrSiO_4 , is widely distributed, being found in India, Madagascar, and New South Wales. It is also plentiful in some of the beach sands of Florida, where it can be concentrated to 60 or 80 per cent of zirconium silicate. It occurs in the form of fine white sand. The analysis of a typical zircon sand is given in Table 27.

The zircon minerals have been used to a limited extent as bricks. Zirconia crucibles are rather extensively used in the laboratory for special melts.

Thoria.—Thoria is a rare refractory oxide. It occurs in the monazite sands of the southern United States. At present it is too rare for general refractory use but has been used for laboratory crucibles of great refractoriness.

Ceria.—Ceria is another refractory oxide from the same source as thoria but is also too rare for general use at present.

7. Silicon Carbide.—Silicon carbide is a synthetic crystalline mineral made in the electric furnace at temperatures between 1780°C . (3236°F .) and 2200°C . (3992°F .) from sand and coke.

TABLE 28. NATURAL MINERALS (Continued)

Material	Formula	Fusion point (°C)	Occurrence	Specific gravity	Hardness
Dunite.....	Mg ₂ Si ₂ O ₆ (OH)		Very rare	3.30-3.36	7
Dysanite.....	(Ca,Ca,Ce,Fe,Na)O·6H ₂ O·Cr ₂ O ₃		Very rare	4.26	5-6
Euxenite.....	Ca ₂ UO ₂ (OH) ₂ ·2H ₂ O		Very rare	4.30-4.39	6-5
.....	2AlPO ₄ ·(Al(OH) ₃) ₂ ·2H ₂ O		Very rare	4.92-4.93	3-5-4
.....	Y(Nb,Ta)O ₃		Very rare	4.98-5.78	5-5-6
Fergusonite.....	(Ca,Sr)[(Ca(OH,F)) ₂ (P,AsO ₄) ₃]		Rare	5.32	5
Ferromerite.....	AlF ₃ ·H ₂ O		Very rare	3.17	3
Fluellite.....	(Ca,Lu,Dy)F ₃		Very rare	5.73	4
Fluocerite.....	Mg ₂ SiO ₄	1910°C. (3170°F.)	Uncommon	3.22-3.27	6-7
Postierite.....					
Franklinite.....	Zn,Fe,Mn)(Fe,Mn) ₂ O ₄		Uncommon	5.09	5-5-6-5
Gadolinite.....	(Al,Fe,Mg,Ti) ₂ Fe ₂ (Fe,SiO ₄) ₂ O ₂		Very rare	4.0-4.6	6-5-7-0
Gahnite.....	ZnAl ₂ O ₄		Rare	4.48-4.60	7-5-8-0
Garnierite.....	Perhaps H ₂ (Ni,Mg)SiO ₄ + H ₂ O very variable		Widespread	2.27-2.87	1-3
Gelskrite.....	(Mg,Fe)TiO ₃	2035°C. (3695°F.)	Rare	3.98-4	6
Gibbsite (hydrargillite).....	Al(OH) ₃		Common	2.3-2.42	2-5-3-5
Goodite.....	HF ₂ O ₂		Widespread	4.18-4.48	5-0-5-5
Goslarite.....	ZnSO ₄ ·7H ₂ O		Rare	1.9-2.1	2-2-5
Granddunite.....	2Na ₂ O·Fe ₂ O ₃ ·8(Fe,Al) ₂ O ₃ ·5SiO ₂		Very rare	2.99	7-5
Graphite.....	C		A few deposits	2.22	1-2
Greencokite.....	CdS		Rare	4.82	3-3-5
Grothine.....	Silicate of Ca, Al, Fe (uncertain)		Very rare	3.08-3.09	
Gummite.....	Doubtful composition, alternative product of uraninite		Rare	5.08	2-5-3
Halloysite.....	Al ₂ Si ₂ O ₅ (OH) ₄ ·H ₂ O	1775°C. (3227°F.)	A few deposits	2.44-2.71	1-2

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CHAPTER VI

THE MINING AND PRELIMINARY TREATMENT OF REFRACTORY MATERIALS

1. *Mining of Clays. Open-pit Methods.*—Many refractory clays are mined by open-pit methods. Usually the bed of clay is covered by an overburden of gravel or earth which may run as thick as 10 to 20 ft. If the thickness of overburden is much greater than 20 ft., it is seldom economical to mine a low-cost clay by this method.

The first process consists in stripping off the overburden in the most economical manner. In small workings, where the overburden is thin, this is done by horse-drawn scrapers; but in larger operations the overburden is stripped with power shovels. In other workings, it is found economical to strip the overburden with dragline scrapers with a capacity of $\frac{1}{3}$ to 4 cu. yd. This type of scraper is very flexible and can be made to cover a large area by using a movable cable anchor. Lines as long as 500 ft. are used; and with a 1 cu. yd. bucket, 20 to 75 cu. yd. per hr. can be moved, depending upon the length of the haul. A typical dragline installation stripping the overburden from a kaolin deposit is shown in Fig. 57.

There are a few locations where water is available in large enough quantities and the draining conditions are sufficiently good to make hydraulic stripping economical.

The method of removing the clay itself varies with the conditions. If the clay is fairly soft, the face may be broken with picks or bars and the broken material loaded by hand into carts or cars, as illustrated in Fig. 58. In the larger plants, however, this method is not economical, and power shovels are generally used, as shown in Fig. 59. The shovel capacity varies from $\frac{1}{2}$ to 2 cu. yd. The larger shovels are chosen not only for their greater capacity but also for their greater strength and longer reach. Caterpillar treads are almost universally used. A 1 cu. yd. shovel will load, under good conditions, 500 tons of clay in an

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8-hr. day. Recently, lighter and more agile shovels are being favored.

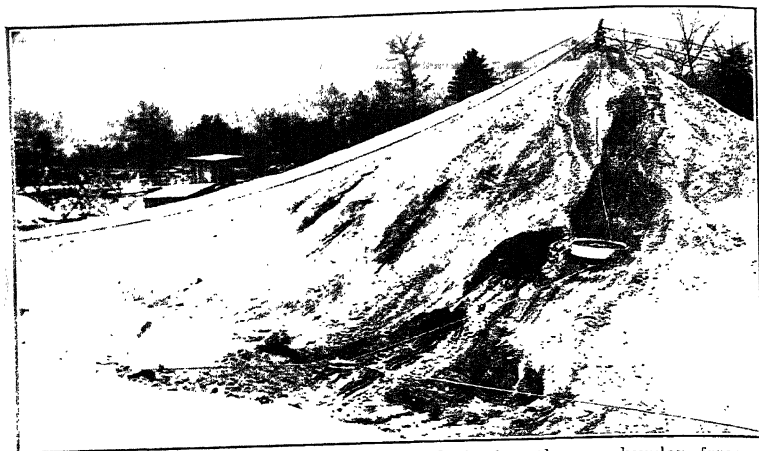


FIG. 57.—A typical drag-line installation. Stripping the overburden from a kaolin deposit. (Courtesy of Sauerman Brothers, Inc.)



FIG. 58.—Breaking up and loading clay into cars by hand.

The softer clays can be taken out with dragline scrapers or bucket excavators. Occasionally wheel scrapers and rotary ditchers are used.

Provided the clay is not too hard and yet is firm enough to hold a permanent face, as in the case of many shales, it has been found economical to remove the materials by a planer, which is

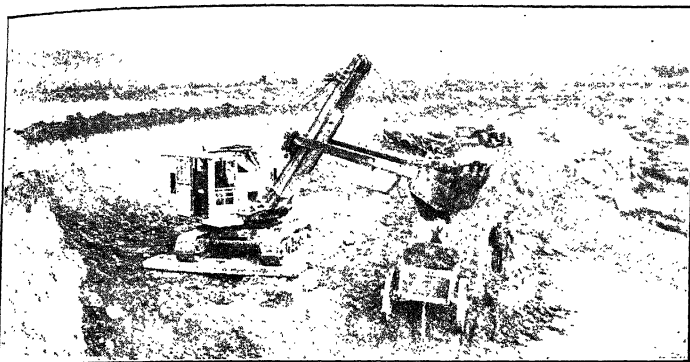


FIG. 59.—Removing clay with a power shovel. (Courtesy of Koehring Company.)

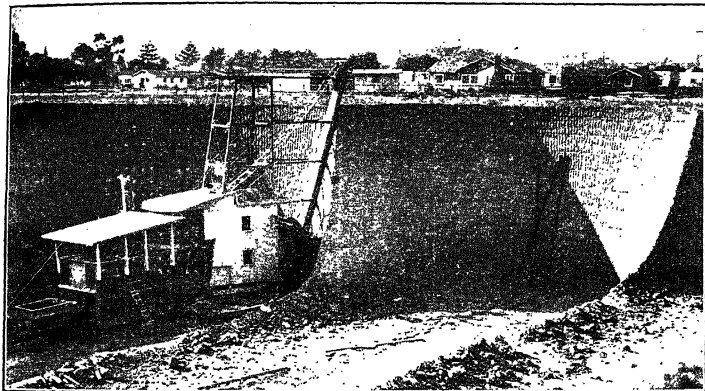


FIG. 60.—Removing clay with a planer. (Courtesy of Eagle Iron Works.)

an endless chain with cutting knives working vertically on the whole face as shown in Fig. 60. This machine has the advantage of removing the material in small pieces and of giving a good average composition by taking the material from the whole face.

The cost of removing the material with a machine of this type is comparatively low, as one man can usually operate it and obtain a production of 200 to 400 tons a day.

In Europe, the endless-chain excavator working from the top of the bank is often used. Although the initial investment is large, the low labor and maintenance cost justifies it on large operations. One man can remove 100 tons per hour with an average-sized machine.



FIG. 61.—A large fireclay pit. (Courtesy of A. P. Green Fire Brick Company.)

In the case of hard clay, it is generally necessary to drill and blast the face in order to obtain small enough pieces to be readily handled. The drilling is done in the smaller pits with hand drills of 1 to 1½ in. in diameter. In the larger mines, however, electric and air drills are used. Recently, portable well drills have been used to a considerable extent to drill deep holes behind the working face so that larger and deeper charges of explosives can be set off. These drills will produce holes from 3 to 5½ in. in diameter, which will allow the use of a considerable quantity of explosive.

When the clay has been loosened from the face, it is loaded into cars or trucks by hand or power shovels. A large fireclay pit is shown in Fig. 61.

Underground Methods.—When the clay deposit is too deep for stripping, underground mining is used. Most of the productive clay veins are from 5 to 15 ft. thick. The room-and-pillar method is generally used, with advance from the entrance, which consists of cutting a mine entry and advancing galleries from that out to the edge of the property. This method has the advantage of not requiring extensive entry development when the mine is started; but it is not so economical as the retreating method, which consists of cutting an entry to the boundary line and then starting the galleries at the farther end. Work is then carried toward the entrance. The pillars can be drawn only where the subsidence of the ground is unimportant. Whenever underground mining is used, it is important to plan out the workings carefully and have a systematic method before starting to mine.

Practically all underground clay is taken out by drilling and blasting. Hand, electric, or pneumatic drills are used, and the lumps of clay are loaded on the car by hand or, in more modern mines, by car loaders.

The same factors of economical mining apply to clay mines as to other mines. In the first place, drainage must be well cared for, as muddy floors and tracks increase the haulage costs as well as make the timbering difficult. Next, the timbering should be well done with generous posts. The tracks should also be graded and kept in good condition, as the haulage cost mounts up when dirty, poorly laid tracks are used.

Clay is usually transferred to the plant on rails with dump cars ranging in capacity from $\frac{1}{2}$ to 6 cu. yd. (Fig. 62). The cars are propelled by steam, oil, or gasoline locomotives or sometimes by cable haulage. In a few cases where the distance from the mines to the plant is considerable and the country is rough, it has been found economical to transfer the clay by aerial cableways. Trucks are coming into more general use than formerly.

It is hard to give any definite figures on the cost of mining clay; but in general, clay can be loaded on cars or trucks from the open pit under the best conditions for 50 cents a ton. Where the overburden is heavy or where hand selection is used, the cost may run as high as \$1 per ton at the plant. In the case of special high-grade clays, the cost may run even higher. It may be said, however, that a great number of plants are getting out their

refractory clays for around 50 cents per ton. In underground mining, the cost varies according to the thickness of the vein, the hardness of the clay, the amount of timbering required, and the distance to the plant—the variation in most cases being from \$1.50 to \$2.50 per ton on cars. It may be mentioned that in many of the underground clay mines, coal is obtained at the same time as clay, which, of course, reduces the total cost considerably.

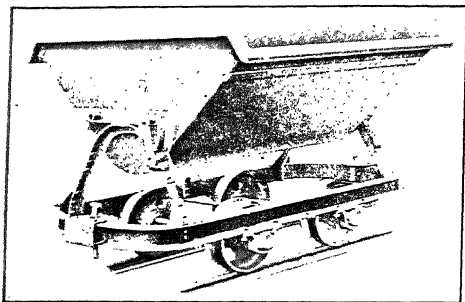


FIG. 62.—Dump car for transferring clay to the plant. (Courtesy of Koppel Industrial Car and Equipment Company.)

2. The Mining of Ganister.—Since the mining of ganister is rather different from clay mining, it will be described separately. The ganister is usually found in flows of loose rock on the mountain sides (Fig. 63). Where the rocks are large, they are broken up by mud capping and blasting; in only a few cases is drilling necessary. The smaller rocks are broken up by sledges into sizes that can be lifted by hand. The broken rock is loaded into dump cars by hand, as some sorting is necessary. One man will load from 15 to 20 tons of rock a day.

The dump cars are trammed either by hand or by locomotive, as the case may be, to a gravity plane and dumped into cars to be lowered down the plane. In a few cases, ganister is carried long distances by railroad to reach the plant.

In some localities, the ganister is obtained from bedrock, because the flows have been used up or because the rock is more uniform. The ledge rock, however, is usually not thought to be so satisfactory as the flow rock, because the soluble constituents have not been leached out by weathering. Others claim that

bedrock gives superior bricks. Regular quarrying methods are used in removing this rock from the hillside. This material will cost 75 cents to \$1.50 a ton on cars.



FIG. 63.—A ganister flow. (Courtesy of Harbison-Walker Refractories Company.)

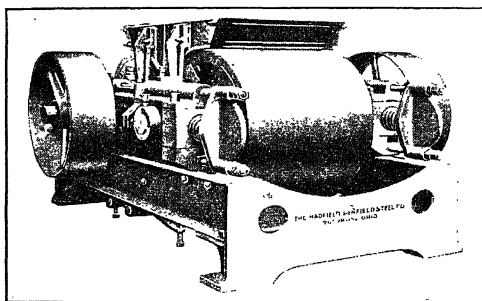


FIG. 64.—A roll crusher. (Courtesy of W. A. Riddell Company.)

3. Preliminary Crushing.—Practically all clay must be crushed before it is taken to the tempering and brickmaking machinery. The softer lump clays are usually passed through single or double roll crushers, which rapidly break down the lumps to sizes small enough for wet pans or pug mills. The wear and

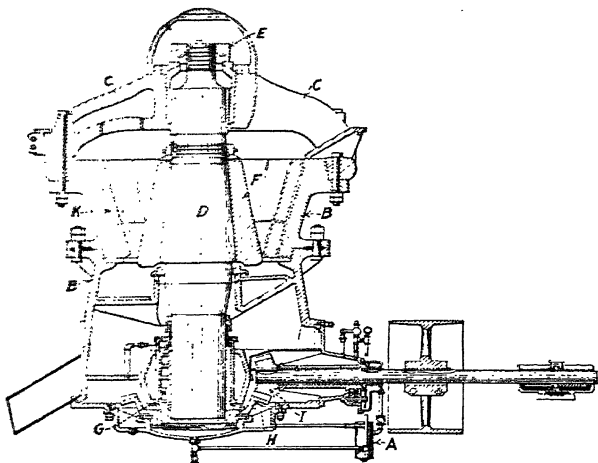


FIG. 65.—Sectional view of a gyratory crusher. (From C. E. Locke.)

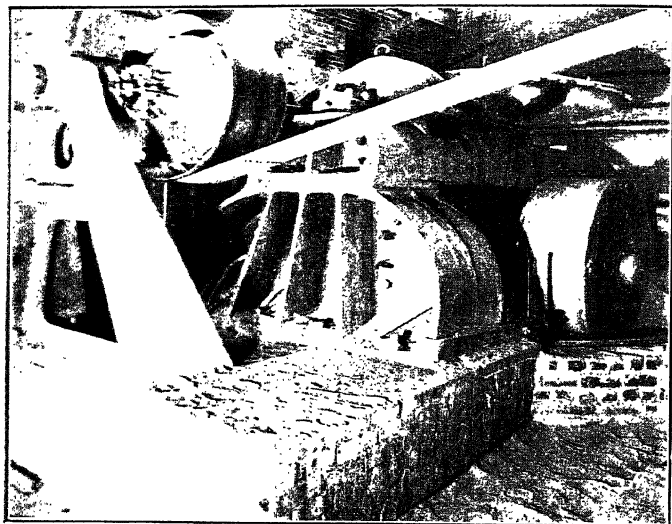


FIG. 66.—A dry pan for crushing flint clay. (Courtesy of Clearfield Machine Company.)

tear on rolls of this type is very small, so the cost of breaking up the softer types of clays is not great.

Jaw or gyratory crushers are usually used for the harder clays, rocks, and grog. They will crush down to 1 in. with capacities of $\frac{1}{2}$ to 500 tons an hour. These crushers cannot be used for the softer clays containing moisture because of packing in the jaws.

Roll crushers (Fig. 64) are used for crushing hard materials from 1 in. down to $\frac{1}{4}$ or $\frac{1}{8}$ in. For materials like grog, the rolls

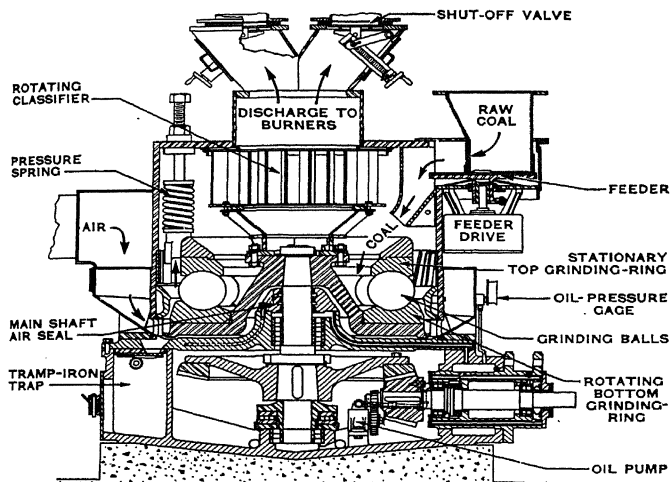


Fig. 67.—Babcock and Wilcox pulverizer. (Courtesy of Babcock and Wilcox Company.)

should be supplied with tires of manganese steel, as the wear is considerable. In order to obtain fine grinding, it is necessary to keep the rolls fairly true cylinders, as flanges tend to form on the ends and the material will be passed through the center uncrushed. Plain rolls should never be used for crushing clays with any moisture, because the material builds up on the rolls and there will be no crushing action.

Gyratory crushers (Fig. 65) are often used for crushing magnetite and ganister. These crushers have a large capacity but will not take such large rocks as jaw crushers.

Dry pans (Fig. 66) consist of a heavy revolving bed in a horizontal position on which the material is fed; two heavy rolls (mullers) rest on this bed with their own weight, crushing the material underneath. The portion of the bed not directly under the mullers is usually supplied with screens or slits so that

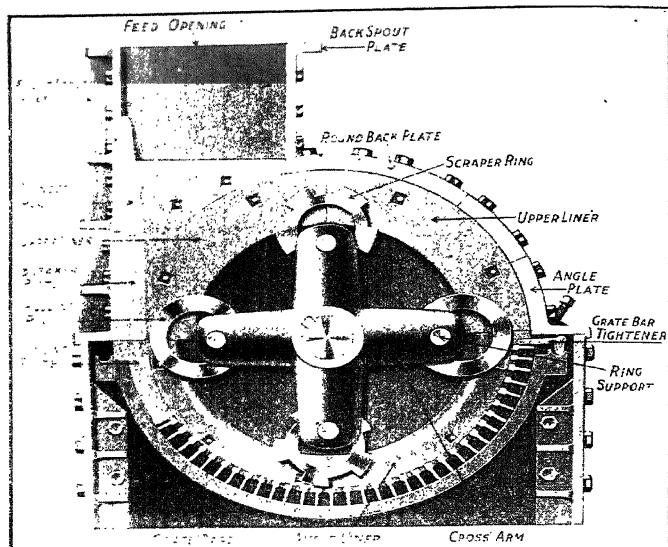


FIG. 68.—Cross section of a ring-roll crusher. (Courtesy of American Pulverizer Company.)

crushed material can pass through, permitting continuous operation. The dry pan is used for grinding flint clay, ganister, and burned grog. Wet pans are similar machines with a solid bottom so that the mix can be ground wet.

For finer grinding, it is often desirable to use crushers of the B and W, ring-roll, or hammer-mill type, as shown in Figs. 67, 68, and 69. Machines of these types will pulverize down to 100 or 150 mesh and can be used for clays with some degree of moisture.

Ball mills are much used for fine grinding. For large production, the continuous type of mill should be selected. The fine

material is removed with an air separator, and the oversize is automatically returned to the mill. A production of several tons per hour of 200-mesh material can be obtained with this type of installation. Even when coarser material is required, the continuous ball mill is often found suitable. In Fig. 70 is shown a typical closed-circuit, ball-mill installation for continu-

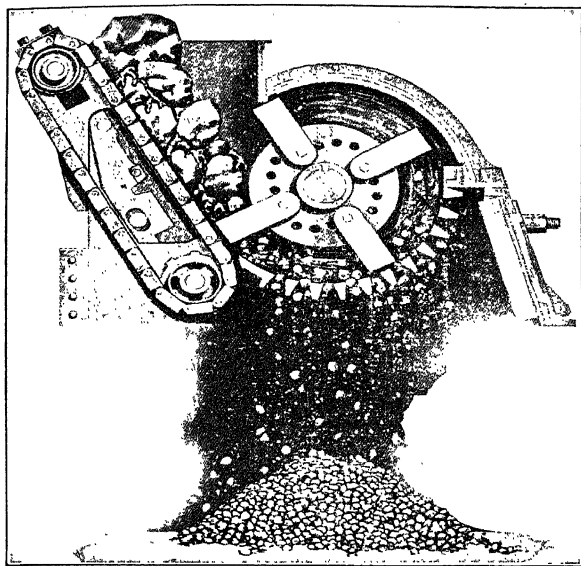


Fig. 69.—Cross section of a hammer mill for fine grinding. (Courtesy of Dixie Hammermill Manufacturing Company.)

ous grinding. The capacities of some ball mills are shown in Table 30. ✓

4. **Screening.**—It is usually necessary to screen the materials being crushed so that the required product can be passed on to the brickmaking machinery and the coarser material returned to the crushers. Various types of screens are used. A revolving screen or trommel is often used for classifying coarser materials (Fig. 71), and screens of several sizes can be applied to the cylinder in order to obtain a product having the desired combination of sizes. ✓

Another type of screen is the shaking screen operated by a cam or eccentric (Fig. 72). Often several layers of screens of

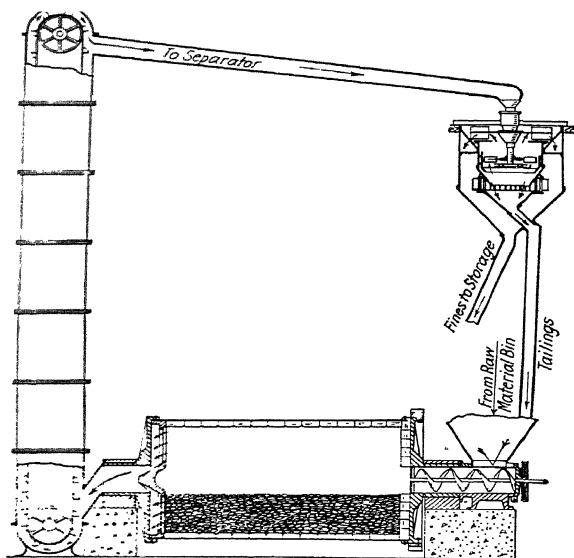


FIG. 70.—Cross section of a continuous ball mill. (Courtesy of Patterson Foundry and Machine Company.)

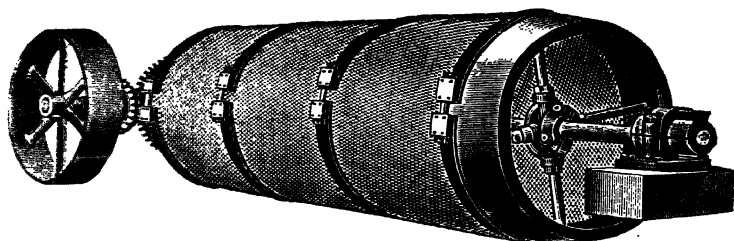


FIG. 71.—A revolving screen for classifying coarse material. (Courtesy of Gruendler Rock and Gravel Crushing Equipment Company.)

various sizes can be superimposed in order to classify a product into a number of different sizes. Pulsating screens (Fig. 73)

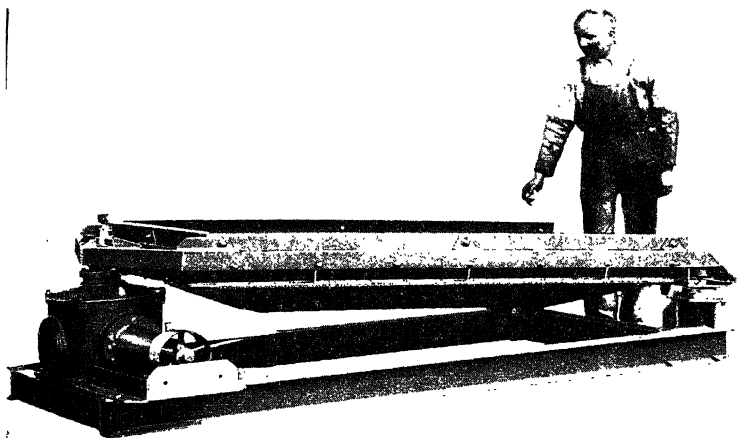


FIG. 72.—A shaking screen operated by an eccentric. (*Courtesy of Orville Simpson Company.*)

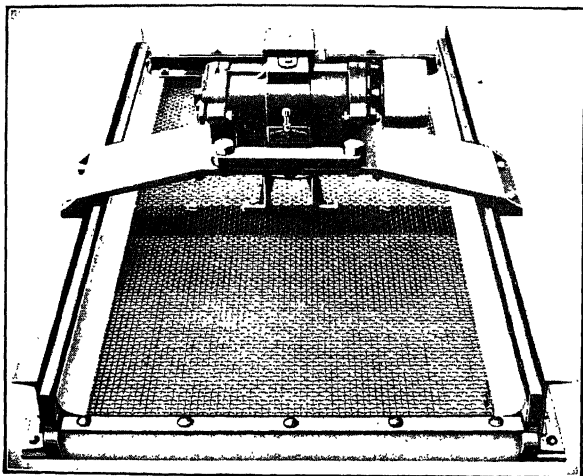


FIG. 73.—A pulsating screen. (*Courtesy of Deister Concentrator Company.*)

vibrate in a direction normal to the plane of the screen and for some purposes have less tendency to clog up. The hummer type of screen is much used, in which the center is vibrated up and down rapidly by electromagnetic means. For screening material below 60 mesh, it has been found desirable to use air separators rather than screens, and very satisfactory classification devices can now be obtained to produce material down to 200 mesh or even finer.

TABLE 30
(From G. F. Metz)

Material	Size and type	Tons per hour	Circuit	Horse-power	Size of feed	Fineness of product	Pebble load, lb.
Silica, dry	7 × 22 ft. tube	3	Closed	210	—20 mesh	98 per cent minus 200 mesh	42,000
Sillimanite	3 × 2 ft. conical	1½	Closed	15	—¼-in. mesh	80 per cent minus 100 mesh	14,000
Grog	5 × 22 ft. conical	4½	Closed	40	—1½-in. mesh	100 per cent minus 4 mesh	6,000
Feldspar	7½ × 10 ft. cylindrical	1.05	Closed	85	—¾-in. mesh	90 per cent minus 325 mesh	

5. Mineral-dressing Methods.—Many refractory raw materials can be purified by simple mineral-dressing methods. As the demand for refractories becomes more exacting and our supplies of the better raw materials less plentiful, concentration methods will be increasingly used.

Tabling.—Minerals of a different specific gravity from the unwanted material with which they are mixed can often be efficiently separated by an air or water table. The raw material is ground fine enough to unlock the individual grains and then passed over an inclined vibrating table which will give a more or less clean separation. Although this method has been used in the past mainly for the treatment of ore minerals, it has been quite successful in the concentration of kyanite from our North Carolina deposits.

Magnetic Separation.—Powerful magnetic separators are now available that will remove all minerals containing even small amounts of iron. These include the iron oxides, sulfides, and more complex minerals such as garnet, hornblende, and micas.

The magnetic method of purification is used quite generally with feldspars and other materials for whitewares, but it has not as yet been used extensively for refractory materials. However, there is opportunity of employing it with some refractories, such as those used in melting glass or enamel frits.

Flotation.—Froth-flotation methods have been developing with such rapidity in the last ten years that many separations can now be made that would have been thought impossible a few years ago. The method, in general, consists in stirring the finely crushed mineral in water with a frothing agent, which provides a multitude of fine bubbles. By selecting the proper agents, it is possible to get a selective action of the bubbles so that they adhere to certain types of particles and float them to the top of the water where they are carried off. Although considerable progress has been made by flotation methods in purification of minerals like feldspar, little has been done yet on refractory materials, but it would seem quite possible that this method would be well adapted to the concentration of chrome ores.

A little laboratory work has been done by flotation methods in removing iron minerals from fireclays, but as yet the results have not been shown to be economically feasible. Nevertheless, there is certainly promise that with further development along this line, second-grade clays can be so beneficiated that first-grade refractories can be made from them.

Chemical Methods.—Chemical methods are too expensive to be used with any refractory materials except special types such as beryllium minerals.^(19,20,22) Although chemical bleaching has been used to remove iron from some of the ceramic and paper clays, the cost would not permit it to be used at present for fireclays.

Electrostatic Separation.—The electrostatic separator has been used to purify both feldspar and kyanite. The method consists in separating one type of mineral from another by virtue of the different attractive forces in a high-voltage field. This is a dry method and should not be particularly expensive except that the particles must be fairly fine before treatment. A patent by Weis⁽²³⁾ describes a method for removing quartz from kyanite.

6. Storage of Clay.—It is usually necessary to store a certain amount of clay to provide for interruptions in mining due to cold or rainy weather or holidays. The amount of needed storage

depends on the length of shutdown in the mining operation. To provide sufficient storage for a large clay plant is rather costly, and it is unusual to store more than a few days' supply.

In many of the ceramic industries, the practice is to weather, or age, the clay supply for a considerable length of time to develop plasticity and disintegrate the lumps; but in the case of refractories, the amount of clay used is so large that this cannot be done economically, and only in the case of special high-grade clays can ageing be resorted to.

Some of the high-grade refractory clays must be shipped a considerable distance by railroad. In these cases, it is desirable to

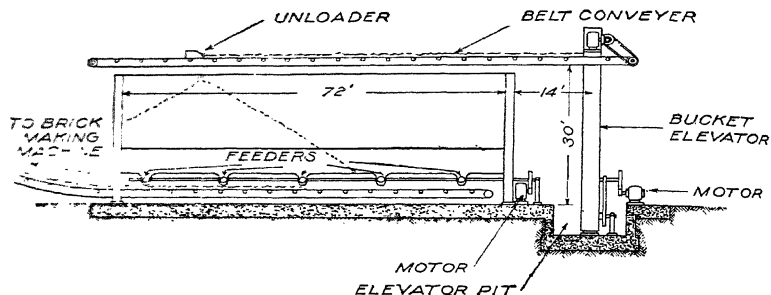


Fig. 74.—A method of handling clay in storage bins.

dry the clay partially in order to reduce the shipping weight. This can be done by storing in open sheds or racks, where the moisture in good weather can be reduced to 5 or 10 per cent, or by passing it through a rotary drier.

Storage bins are made in various styles. Some are cylindrical bins having conical bottoms; others are of a rectangular shape with a V bottom with provision for removing the clay from any portion desired (Fig. 74). The clay is usually put in the bin with a bucket elevator, but other handling methods such as grab buckets are occasionally used.

When crushed materials such as clay or grog are to be stored, precautions must be taken to prevent segregation of the material in the bin. In nearly all manufacturing processes, it is highly desirable to have the crushed materials of a proper and uniform screen analysis. When the material from the crusher falls into

the bin, the larger particles roll to the outside and the finer ones build up into a central cone. The material drawn from the bottom of the bin will contain at first mostly fine and later mostly coarse material. This segregation can be minimized by a num-

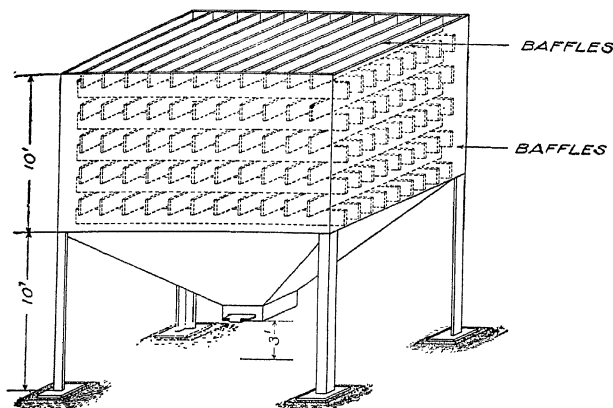


Fig. 75.—Baffles for the prevention of segregation in bins.

ber of methods. One consists in moving the point of supply over the surface of the bin so that no cone can form. Another consists in a number of vertical vanes in the bin to prevent the heavy particles rolling to the outside of the bin (Fig. 75).

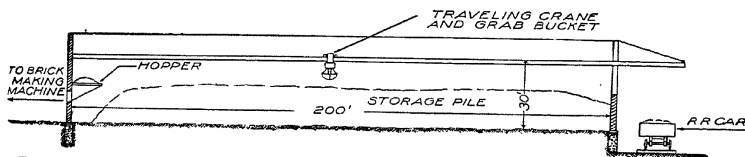


Fig. 76.—An overhead crane and grab bucket for handling clay in storage.

In some cases, clay is stored in open pits or on floors, from which it is handled usually with a locomotive crane and grab bucket or by a dragline scraper. In other cases, the clay is stored in sheds, and the handling is done by an overhead crane and grab bucket (Fig. 76). This gives a very flexible arrangement, as the clay can be dropped on to a conveyor to be taken

directly to the crushing or mixing machinery. The clay-storage system of a modern refractory plant is shown in Fig. 77.

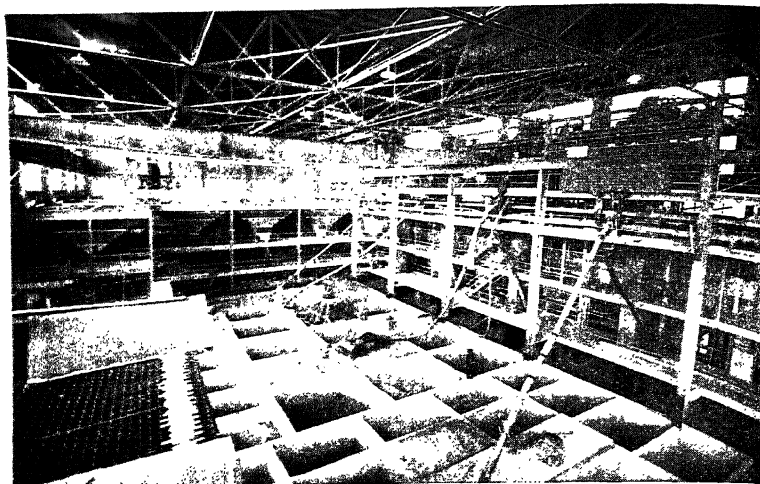


FIG. 77.—A modern storage system. (Courtesy of A. P. Green Fire Brick Company.)

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CHAPTER VII

MOLDING METHODS

✓ **1. Workability of Clay.** *Types of Flow.*—Before entering into the discussion of workability of clays, it will be well to review a few definitions as adopted by the Society of Rheology.^(36a)

Fluid: A substance that undergoes continuous deformation when subjected to any system of finite shearing stress.

Solid: A substance that undergoes permanent deformation or rupture only when subjected to a system of shearing stresses that exceed a certain minimum value.

Simple (Newtonian) Liquid: A liquid in which the rate of shear is proportional to the shearing stress (for laminar flow).

Complex (Non-Newtonian) Liquid: A liquid in which the rate of shear is not proportional to the shearing stress (for laminar flow).

Elastico-plastic Solid (the Clay-water System): A solid that obeys the law of an elastic solid for values of the shearing stress below the critical stress corresponding to the elastic limit in shear and that deforms plastically when the shearing stress exceeds that value.

Viscosity: In a simple liquid, the constant ratio of shearing stress to rate of shear.

Plasticity: That property of a body by virtue of which it retains a fraction of its deformation after the deforming stress is zero.

Elasticity: That property of a body by virtue of which it recovers its original size and shape after deformation.

Thixotropy: That property of a body which causes a decrease in shearing stress with time at a constant rate of shear.

Rheopexy: That property of a body which permits agitation to accelerate the setting up of a gel.

Dilatency: That property of a body which causes an increase in shearing stress with time at a constant rate of shear.

Water alone behaves as a simple liquid; but as anisotropic particles are added to form a suspension, the behavior of the liquid becomes complex owing to the tendency of the particles to orient themselves in the direction of the lines of shear. The greater the rate of shear the more closely the plates will line up with the stream lines and the more closely will the apparent viscosity approach that of water.⁽⁴¹⁾ It is believed that a suspension of

fine spherical particles at low concentrations will behave like a simple liquid, but no experimental proof of this has been offered.

When the concentration of clay reaches a certain value, perhaps 1 per cent, interference effects will be set up between the particles⁽³⁹⁾ so that a finite force is needed to initiate the flow; in other words, we have a gel structure. The finer and more elongate the particles the smaller the proportion of solid material there is needed to form a gel. In the case of bentonite particles of 10 to 20 μ , a gel formation is observed with a concentration of only 0.1 per cent (by weight) of solid.⁽³¹⁾ The reason for this is supposed to be that the small platy particles have a strong attraction for the polar water molecule and build around themselves a hull of bound water of considerable size. These hulls are probably ellipsoids rather than spheroids and form, on standing, a loose network of interfering particles with a finite rigidity. A gel of this kind when agitated will break down reversibly and produce the condition of thixotropy. It should be remembered that whenever a concentration is reached sufficient to require a finite stress to initiate motion, the liquid changes to a plastic solid. Without exception, plastic solids are two-phase systems: hard particles in a softer medium.

In considering the clay-water system, it is usual to separate it into two parts: the slips of low clay content and the plastic masses of high clay content. This is done (1) because industrial processes utilize these two consistencies in separate ways and (2) because the intermediate region between the two is so hard to handle that tests are difficult; at the same time, there is every reason to believe that there is a continuous change in properties with water content over the whole range. In the following discussion, the slips will be considered first and then the plastic masses.

Clay Slips.—The variables that influence the properties of a clay slip are chiefly

1. Particle size
2. Particle shape
3. Adsorbed ions
4. Organic matter
5. Type of clay mineral
6. Concentration of solid
7. Type and amount of deflocculent

The most interesting properties of the slip are the specific gravity, or solid concentration; the apparent viscosity; and the hydrogen-ion concentration, or pH.

Figure 78 shows a typical curve of shear rate versus shear stress for a kaolin slip. The slip is evidently a plastic solid because a finite force is needed to start the flow.

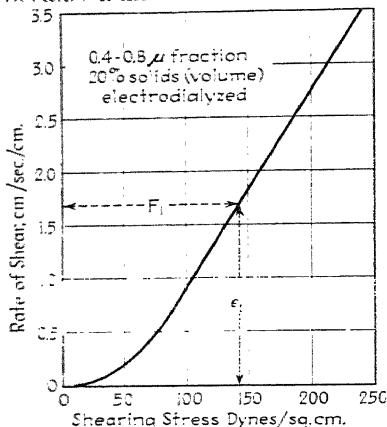


FIG. 78.—Flow relations in kaolin suspension.

This is the principle of deflocculation, which permits fluid slips with low water content. The exact mechanism of deflocculation is not clearly understood at present, but it is believed that free OH ions over and above those absorbed on the clay are required to lower the particle charge and thus minimize the attraction forces between the particles, as discussed by Johnson and Norton.^{65a} These OH ions can be produced by the ionization of bases like NaOH or by the hydrolysis of salts like Na_2SiO_3 . The positive ion accompanying the OH ion must be monovalent; therefore calcium or magnesium salts will not deflocculate. Some of the recent work in colloidal chemistry⁽³²⁾ would indicate that the suspended particles are in equilibrium between a repulsion and attractive force and that this equilibrium is varied by added ions.

Other factors such as organic matter⁽³⁵⁾ and particle shape⁽⁴¹⁾ are undoubtedly important, but at present there is not enough information on which to base any conclusions.

We speak of the apparent coefficient of viscosity at any given rate of shear ϵ_1 as the ratio $F_1/\epsilon_1 = \eta$, where F_1 is the shearing stress.

Figure 79 shows the influence of particle size and amount of ions added to a slip of constant solid content. The various-size fractions were separated from a kaolin with a centrifuge and cleaned. Then definite amounts of sodium hydroxide were added in milliequivalents per 100 g. of dry clay. The enormous reduction in apparent coefficient of viscosity on adding sodium hydroxide is evident in all

Plastic Masses.—Turning now to the plastic masses with a high enough yield point to resist gravity forces, it is well to consider some fundamental principles. In general, the three-component

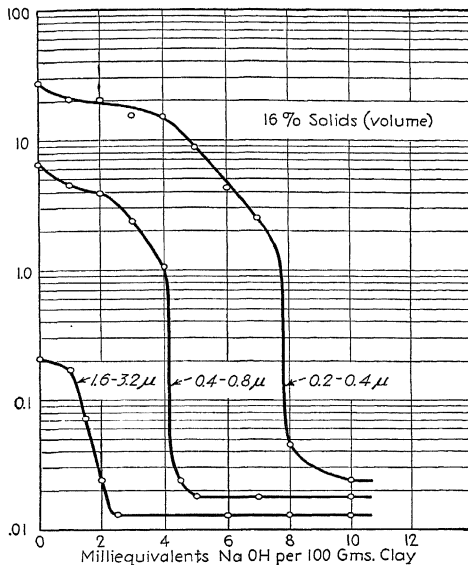


FIG. 79.—Viscosity of kaolin slips.

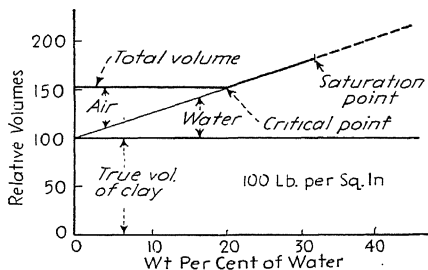


FIG. 80.—The air-water-clay system under low pressure.

system, clay-water-air, may be expressed in the somewhat conventionalized volume diagram for a low molding pressure shown in Fig. 80. Such a diagram is made up by thoroughly

mixing and kneading clay and water batches of successively increasing water content and molding each in a cylindrical steel die at the given pressure. Provision is made for the escape of excess water. The wet and dry volume and the wet and dry weight will readily allow the volumes of air, water, and clay to be computed, provided the specific gravity of the clay is known.

As the amount of water is increased, the total volume of the mix, which originally consisted of clay and air, shows little change as the pores become filled. At the critical point, all the voids in the clay are filled with water and the air phase vanishes. As

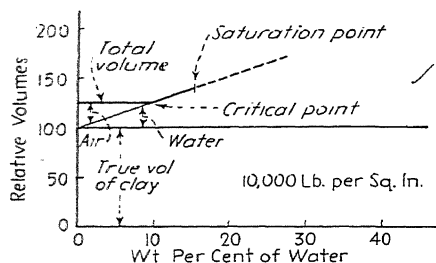


Fig. 81.—The air-water-clay system under high pressure.

the water is increased still further, the particles are separated by a film of increasing thickness until the maximum for stability is reached at that pressure. This may be termed the "saturation point." If more water than this was originally in the clay, it will be squeezed out in permeable pressing.

The critical point is a very important one, as above this point the mass shrinks on drying owing to the removal of the water films, as discussed in Chap. VIII. The thicker and more numerous the films per unit length of clay specimen the greater the shrinkage. Below the critical point, there is little or no drying shrinkage. The critical point also is the dividing point between the consistency of a damp powder and a homogeneous plastic mass.

At a higher molding pressure such as would be obtained in a dry press, for example, the diagram would appear as shown in Fig. 81. Both the critical and saturation points are moved to low values of water content.

There are often slight exceptions to the simplified diagrams shown here. For example, the total volume sometimes decreases

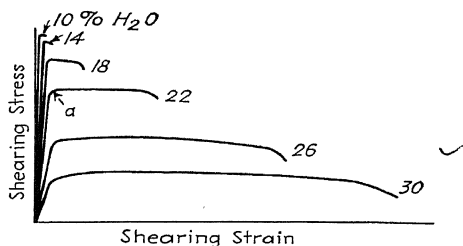


FIG. 82.—Flow properties of a plastic body.

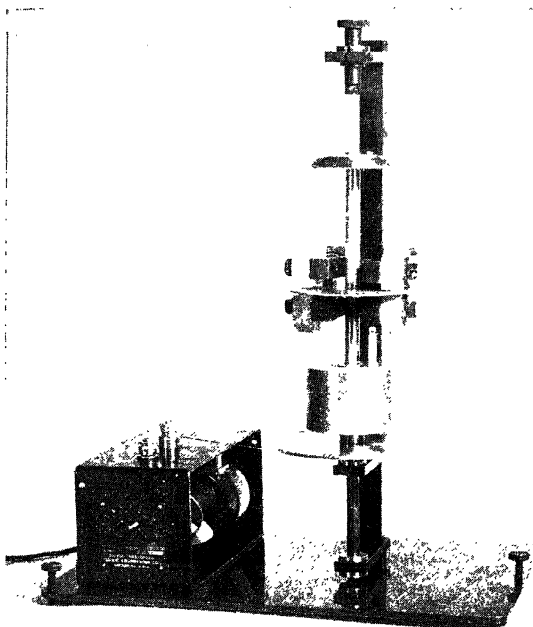


FIG. 83.—Modified MacMichael-type viscosimeter.

slightly as water is added up to the critical point, for the water acts as a lubricant and allows closer packing. On the other

hand, if the clay contains bentonite, the particles of which swell in water, drying shrinkage may occur below the critical point.

The flow characteristics of plastic masses are shown in Fig. 82 for various water contents.^(29, 38, 46) The flow is elastico-plastic; and as the water increases, the yield point becomes lower while the maximum strain becomes greater.

Measurement of Workability.—The consistency of slips is best measured in a concentric cylinder viscosimeter, such as that developed by MacMichael. A modified instrument is shown in Fig. 83. In this instrument, an outer cup, which can be revolved on a vertical axis at various speeds, holds the slip. An inner cylinder is suspended coaxially with the outer cup on a torsion wire that measures the torque. By suitable calibration with standard sucrose solutions, the dial on the wire can be made to read the apparent viscosity coefficient of the slip in poises. In the case of slips, we have only to measure the apparent viscosity coefficient at various rates of shear to obtain all the desired mechanical properties.

In the case of plastic masses, not only the deforming force is required but also the maximum deformation at fracture. The most useful method for evaluating the workability factor is to twist a hollow cylinder and obtain the stress-strain diagram in pure shear. A satisfactory machine for accomplishing this, which was developed some time ago in the Ceramic Laboratory at the Massachusetts Institute of Technology,⁽³⁸⁾ is shown in Fig. 84.

The specimen *B*, with its brass end pieces, is clamped in the torsion head *C* by means of a wedge, as shown more clearly in the detailed sketch. This offers a simple and secure locking device which prevents any backlash during the test. The torsion head is rotated by the motor *D* through the reduction gear *E*, the flexible couplings *F*, and the gears *G*. The motor and reduction unit are mounted on spring suspensions *H* to prevent any vibration from being transmitted to the remainder of the apparatus. This drive gives a constant speed with sufficient power for any of the tests with plastic materials. The speed of the motor can be altered by the voltage regulator *I*, and its direction is reversed by switches *J* and *K*, which independently control the separate field coils. In addition, the speed may be changed by various sets of gears at *G*.

The angle of rotation of the specimen is recorded by the steel tape *L*, one end of which is wound around a drum on the torque

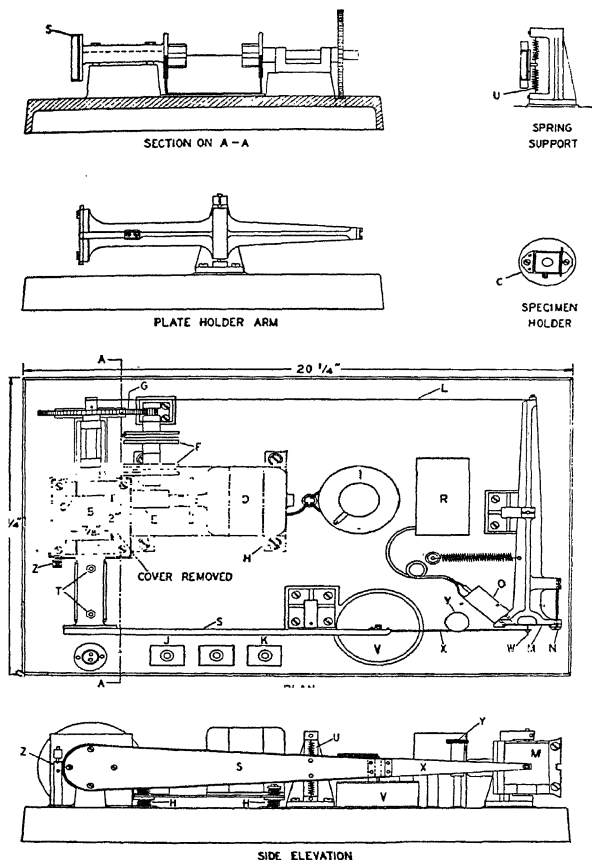


FIG. 84.—Apparatus for measuring workability. (Courtesy of the American Ceramic Society.)

shaft and the other attached to the plate-holder arm so that the angular rotation is proportional to the movement of the smoked

plate *M*. This plate is held in a spring clip *N* and is illuminated from the back by the light *O* supplied by the 6-volt transformer *R*. This illumination is necessary for close observation of the stylus in relation to the zero line, as will be described later.

The torque on the specimen is measured by the deflection of the light aluminum arm *S*, which is pivoted on the center line of the specimen with the flexible steel emery knife edges *T*. The deflection of the end of the arm is, therefore, free from any

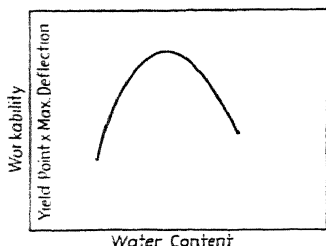


FIG. 85.—Workability of a plastic body vs. water content.

friction effects and is proportional to the torque. In the case of the stiffer materials, the springs *U* are necessary to supplement the knife edges. Under these conditions, the vertical movement of the end of the arm *S* is proportional to the torque for the small angles employed. The movement of *S* is controlled by the dashpot *V*, filled with a light oil of a viscosity to give critical damping. Such

damping is necessary when rapid movements of the arm occur in the initial portion of the stress-strain diagram.

The recording of the diagram takes place on the smoked glass plate *M* by means of a pointed steel stylus *W* held against the plate lightly by the thin steel spring *X* so that very little friction results. The stop *Y* allows the stylus to be removed from the smoked-glass plate after the completion of a record.

Referring back to Fig. 82, typical stress-strain diagrams of plastic clay at various water contents will be seen. The points to be noted are the yield point *a*, the twist at the breaking point, and the maximum torque. No one figure will represent the workability, but a high yield point and high deformation will give the best value. Roughly, the product of the yield point and the maximum deformation may be taken as the workability. If this product is plotted against water content, it will show a maximum value at the consistency of best workability,^(29,44) as shown in Fig. 85.

The stress-strain diagram is altered by changing the rate of shear,⁽³⁸⁾ so it is well to perform the tests at a shear rate comparable with that encountered in a particular forming process.

Clay masses are elastic up to the yield point only under rapid deformations.

Numerous other methods have been mentioned for measuring workability, such as the orifice flow of Stull and Johnson,⁽⁴⁵⁾ the tension test of Hyslop,⁽³⁰⁾ and the cylinder-compression method of Roller,⁽⁴²⁾ as well as the many impression methods similar to the Vicart needle. *M. S. M. P.*

Mechanism of Workability.—If we postulate that workability is associated with a high yield point and a large plastic deformation, it is necessary to assume that the workable material must have particles that (1) hold themselves together strongly and (2) allow a large relative sliding movement of these particles without rupturing the bonding medium. The first condition could be fulfilled by interlocking particles; the second by particles in a large amount of fluid; but to fulfill both demands rather peculiar conditions. There must be a thin and strongly attracted liquid film between the particles to produce a high yield point, and the particles themselves must be able to slide one upon the other for a considerable distance without either rupturing the liquid film or causing the particles to interfere. These conditions can be satisfied to a large extent only by small particles that have a perfect cleavage into large faces, and these faces must have a strong attractive force for the liquid.⁽²⁹⁾

An examination of the natural minerals indicates that the clay minerals alone satisfy the preceding conditions. They are small in size; they form platelike particles with two flat and parallel faces; and due to the OH groups, they have a strong attraction for the polar water molecule. The work of Wilson⁽²⁹⁾ indicates that other minerals in water show a lesser degree of workability according to the extent to which they fulfill the required conditions. Graphite forms small platelike particles but has little attractive force for the water molecule and therefore gives a feeble workability owing to the indefinite yield point as shown in Fig. 86. Minerals closely associated with the clay minerals in the form of plates but with less attraction for the water film, such as goethite, gibbsite, and talc, show a small but

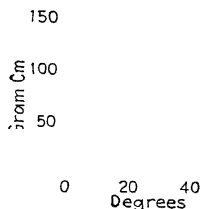


FIG. 86.—Stress-strain curve for graphite and water. (E. O. Wilson, Courtesy of American Ceramic Society.)

Definite yield point (Fig. 87). They therefore have some workability but appear of flabby consistency. The increased torque with increasing shear is probably due to particle interference. The least workable minerals are those showing no definite cleavage and little attraction for the water film. An example of this is ground quartz, which has no workability, as shown by the stress-strain diagram in Fig. 88. Owing to interlocking of the jagged particles, a high yield point is attained but no plastic flow whatever. At higher water contents, the yield

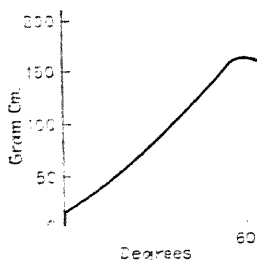


FIG. 87.—Stress-strain curve for gibbsite and water. (E. O. Wilson, *Courtesy of American Ceramic Society.*)

point would be zero.

With the omission of the nonaqueous plastic masses, such as plasticine and putty, the picture given above seems to be a very reasonable one, but much more research is needed to clear up the many obscure details. Further work such as Wilson's, on carefully fractionated specimens with controlled adsorbed ions and organic matter, would be very illuminating.

2. The Casting Process. Casting Slips and Deflucculents.—The casting slip is a mixture of clays, nonplastics, and defloculents proportioned to give the proper physical properties. A good slip should have in so far as possible the following properties:

1. A low enough viscosity to flow into the mold readily

2. A high enough specific gravity to prevent settling of the nonplastic

3. Ability to drain cleanly (in drain casting)

4. Capable of giving sound casts (in solid casting)

5. Stability of properties with ageing

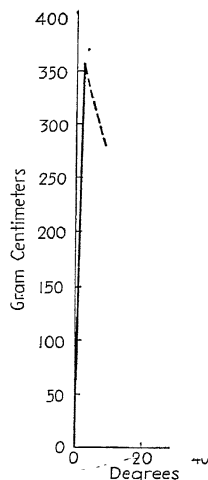


FIG. 88.—Stress-strain curve for quartz and water. (E. O. Wilson, *American Ceramic Society.*)

6. Quick release from the mold after casting
7. Rapid casting properties
8. Low drying shrinkage after casting
9. High dry strength after casting
10. High extensibility in the partly dried condition
11. Freedom from entrapped air

Considerable experience is needed to make up a good casting slip, as we do not have enough basic data to work it out on a scientific basis. In other words, casting is an art at present. In general, there are two types of casting slips: a fine-grained slip for casting refractory porcelain and crucibles and a heavy grog slip for solid casting glass pots, tank blocks, and shapes. The proper selection of the clays for a good slip is now a matter of trial and error. The coarser clays give rapid casting, and the finer ones strength. A number of deflocculents are used such as soda ash and sodium silicate,⁽⁵⁶⁾ as well as sodium tanate⁽⁵⁷⁾ and special ammoniacal⁽⁶⁵⁾ deflocculents. The amount of deflocculent should be kept as low as possible in order to prevent fluxing by too much alkali.

A formula for a typical casting slip for a refractory porcelain body is given in Table 31.

TABLE 31

	Per Cent
China clay.....	43
Ball clay.....	5
Flint.....	34
Feldspar.....	18

Sodium carbonate and sodium silicate in equal parts are added to just reach the minimum viscosity. About 0.1 per cent based on the dry weight of solids is required. The specific gravity should be about 1.78, and firing temperature 2600°F. (1430°C.).

During the last few years, much interest has been shown in methods for casting refractory oxides without a clay addition. This operation can be successfully accomplished in a number of ways. If a fused oxide, such as magnesia, zirconia, or thoria, is ball milled in dilute acid for several hours and then used at once, simple articles like crucibles and tubes can be cast directly in plaster drain molds.^(57a, 63a) Coating the molds with talc, pyrophyllite, or zinc stearate may be necessary to permit release.

Many of the acid ground slips are unstable and cannot be stored. The U.S. Bureau of Standards has made excellent slips of magnesia milled in absolute alcohol for small castings.

Castings have been made from nonplastics supported in slip form by organic materials, such as a dispersion of rubber latex.

For casting heavy tank blocks, a high-grog slip gives good results. In all cases, deairing the slip in a vacuum gives sounder and denser casts. The proper sizing of the nonplastic is also important in all coarse-grained slips. Casting slips with as low as 15 per cent water may be made by careful selection of materials and proper deflocculation. A typical slip, having a water content of about 25 per cent, is given in Table 32 by Wright and Fuller.⁴⁷

TABLE 32.—TYPICAL HIGH-GROG-SLIP FORMULA

	Per Cent
Vitreous grog.....	48.00
Kentucky ball clay No. 4.....	11.00
Tennessee ball clay No. 5.....	11.00
Kaolins (equal parts Florida, Georgia, and North Carolina).....	23.40
Feldspar.....	6.40
Sodium silicate.....	0.12
Soda ash.....	0.09

Molds.—Space is not available here to go into the question of mold making to any extent, but a few of the essential facts may be stated. Practically all the ceramic casting is done in plaster of Paris molds made from a mixture of good pottery plaster and water. In a modern plant, the mixing is carried out with a high-speed mechanical mixer, as it is found that this method gives a more uniform mold and one freer from bubbles. A good average composition for a casting mold would be 36 lb. of water and 40 lb. of plaster, which is allowed to soak for 2 min. and stir for $3\frac{1}{2}$ min., after which it is poured at once into the case or forms. Of course, the new batch of plaster must be prevented from sticking to the solid plaster case into which it is poured, and general practice in the ceramic industry is to use a thick solution of soft soap and water to coat the surface of the solid plaster against which new plaster is to be poured. Apparently the soap forms an insoluble calcium compound on the surface of the plaster which gives a polished surface with good wear resistance;

consequently it is possible to cast a great many hundred molds from one case without losing accuracy.

The molds are made for two types of casting: The first is called a "drain casting," and the second a "solid casting." In the first type, the slip is poured into the dry mold until it is completely full and allowed to stand for a sufficient length of time to build up on the dry plaster a layer of body of the required thickness, as shown in Fig. 89. This may take anywhere from five minutes to an hour or more, depending on the type of piece. As soon as the required wall is built up, the liquid slip in the center is drained out, leaving a uniform casting. The top edge of the mold has to be designed in such a way that a true upper edge can be obtained readily on the finished piece. As shown in Fig. 89, a spare is generally used, so the level of the slip is somewhat above the top edge.

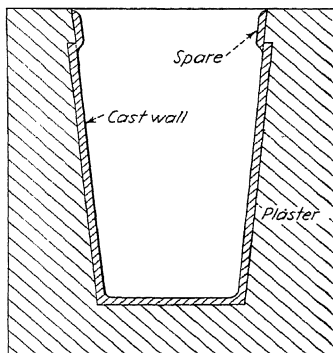


FIG. 89.—Section of mold after draining.

After draining, the body is trimmed with a vertically held knife tangent to the plaster surface, which should project out just to the thickness of the cast wall. In this way, a true edge can be quickly obtained.

When the slips contain large particles of grog, it would be obviously impractical to make drain castings, because the inner surface would be extremely rough. In this case, it is usual to make a solid casting in a mold, somewhat as shown in Fig. 90, for casting saggars. Here the slip is poured into the center of the mold and fills the annular space, rising up into the vent holes. A head of slip must be kept on the mold at all times because the solid casting gradually shrinks as the slip becomes solid and additional material has to be supplied to take up this shrinkage. In other words, the design for a mold for a solid casting is identical in principle with the design of molds for casting metal, where the gate has to be of sufficient volume to supply metal while the piece is solidifying.

Plaster molds naturally are comparatively soft and will wear after long use. It is a little difficult to give any exact figures on the life of a plaster mold, as this will depend on many factors. A mold for casting a fine-grained slip by the drain method may be made to give a hundred casts quite satisfactorily if no fine detail is involved. Of course, the molds for casting grog bodies must take more wear and tear, but here we can afford to have considerable wear before the mold is discarded. The alkali

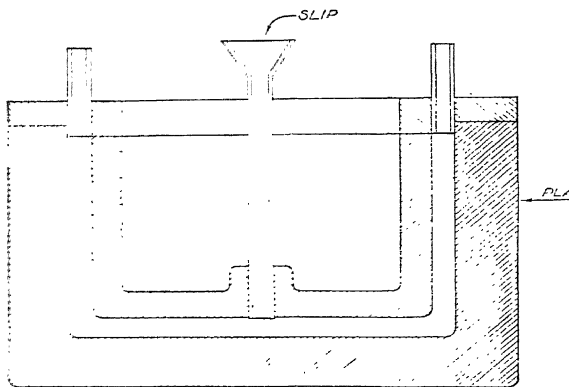


FIG. 90.—A mold for solid casting.

used as a deflocculent in the slip will cause some deterioration of the mold, due to the salts being drawn into the mold where they become concentrated. It has been found that some of the organic deflocculents give a considerably greater mold life than the sodium carbonate and sodium silicate usually employed.

Methods of Casting.—The casting slip is made up by blunging the solid ingredients with water and a deflocculent. The slip is usually agitated for a considerable length of time in order to be sure that the clay is thoroughly wet and that the air bubbles are well removed. In some cases, the blunging is done with a high-speed mixer; in other plants, it is carried out in large vats with a slow-speed paddle. The fine-grained bodies for drain casting are generally made up in two stages; *i.e.*, the material is blunged up first with water to a rather thin consistency, passed through a screen of around 80 to 120 mesh and over a

magnetic separator, and then filter-pressed to remove most of the water. The filter cakes are then reblunged with deflocculent^(49, 53, 57) and some of the screened slip to make up the final slip. These steps are taken in order to make a sufficiently fluid slip to screen before the deflocculent is added. In the case of coarse-grained bodies, the slip is usually made up directly with the deflocculent.

The slip is often handled by pipe lines so that it can be fed under pressure to each casting bench, allowing the workman to fill his molds rapidly. In the case of the heavier slips, this cannot be readily done and the material is handled in hoppers. Sometimes it has been found desirable to deair the slip in a vacuum before casting in order to make a more dense structure. Some manufacturers prefer to use their slip at an elevated temperature, perhaps 90°F.

The handling of the scrap trimmed from the cast pieces presents quite a problem, as it must be mixed back with the original batch in such a way as not to disturb the deflocculation.

M. Sub
3. The Soft-mud Process.—The soft-mud process for making bricks, one of the oldest of all molding processes, has been used for making all types of brick from the earliest times. Although machines are available for making soft-mud bricks, they are used very little in the refractories industry, being confined to the manufacture of building brick; consequently here we will discuss only the hand-mold process.

The hand-mold method is used for making brick in both small and medium shapes. This process is particularly suitable for making certain types of special shapes, particularly intricate ones where the mold cost would be prohibitive by other processes. However, the total shrinkage is high, running from 6 to 12 per cent. Figure 91 shows a flow sheet of a typical hand-mold process. The individual clays are taken from the storage piles and crushed in a jaw crusher or dry pan, after which they are placed in overhead bins so that they can be removed by gravity. In one process, the clays are proportioned in a batch and then fed to a wet pan (Fig. 92), where the whole mass is ground to the proper degree with water. Another method separates the clays into more or less definite-size fractions which are then mixed together dry and the water mixed in either with a wet

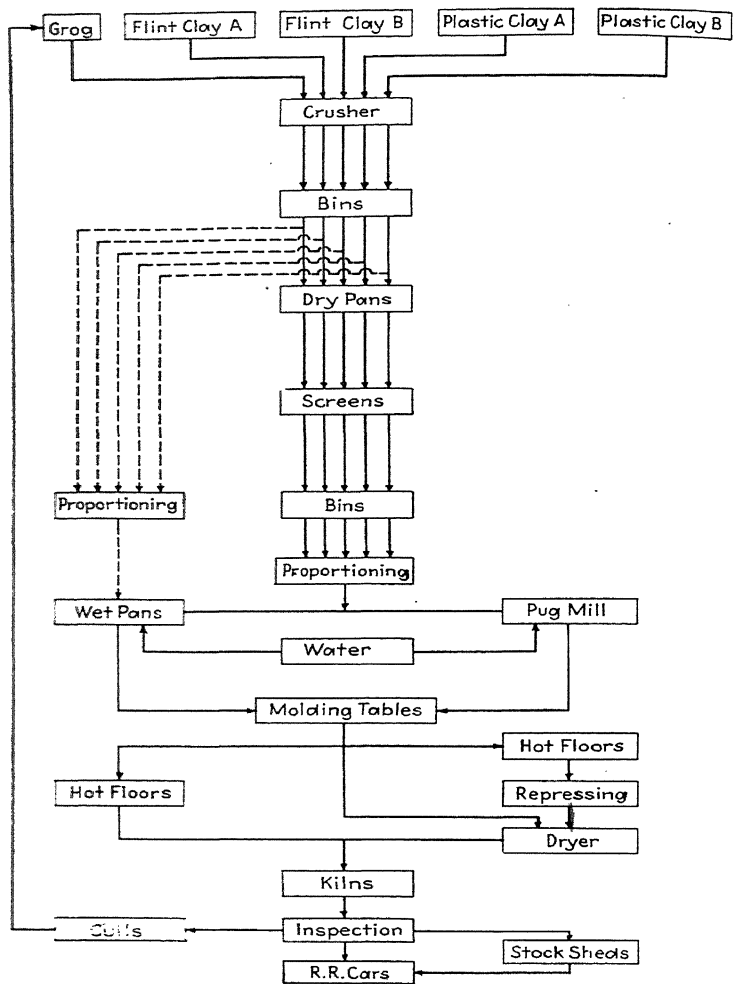


FIG. 91.—Flow diagram for the manufacture of hand-made brick. (Courtesy of S. M. Phelps, American Refractories Institute.)

pan or with a pug mill (Figs. 93 and 94). The proper amount of water must be added to give a mix of the right consistency.

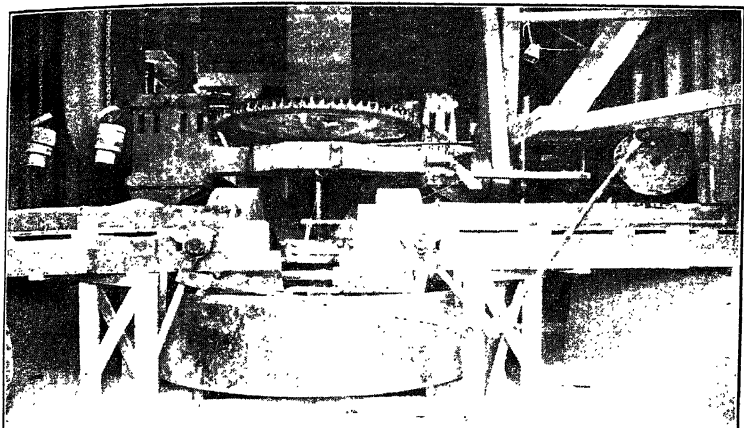


FIG. 92.—A wet pan for crushing or mixing. (Courtesy of Clearfield Machine Company.)

A change of as little as 1 per cent can usually be detected by the molders.

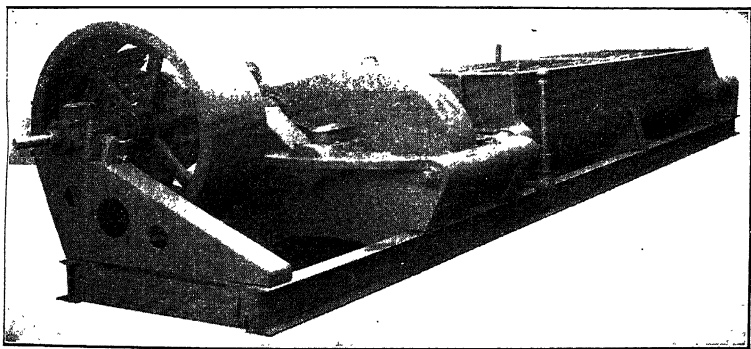


FIG. 93.—A pug mill for preparing clay. (Courtesy of E. M. Freese and Company.)

The plastic mix is taken from the mixing machine to the molders' table located near the hot floor. The hand molder

rolls a homogeneous slug of clay, sometimes called a "walk," of a little more than the volume of the mold. This slug is then lifted over the head and thrown with considerable force into the mold, where the inertia forces it into every corner. If more than a few pieces are to be made, the mold is usually made of hardwood lined with $\frac{1}{16}$ -in. steel sheets. Sometimes loose pieces line the mold, which may be a single mold or may be divided by partitions to make a number of units.

The clay is prevented from sticking to the mold by dusting the wet mold with sand between moldings or oiling it with brush

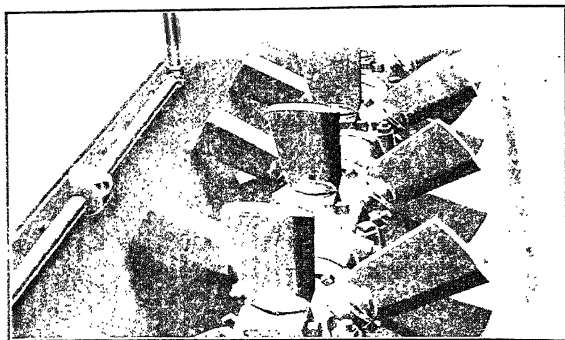


Fig. 94.-Interior of a pug mill. (Courtesy of E. M. Freese and Company.)

or spray. When the mold has been filled, it is violently bumped to consolidate the clay; then the excess portion is cut off with a wire, and the top slicked down. In the case of the larger shapes, it is necessary to fill the mold with several walks of clay, but care must be taken to avoid lamination. The mold is then dumped either on the hot floor or on a pallet, and the piece is allowed to dry.

The fine series of photographs in Fig. 95 shows the steps in molding a shape by this process. Usually, hand-molded pieces in the standard sizes are hand repressed; *i.e.*, the hand-molded piece with a water content for stiff-mud consistency is placed in an oiled-steel die box (Fig. 96) and pressed to give an accurate shape and put on the brand.

Perhaps 5 per cent of all standard-shape fireclay refractories are now made by the soft-mud process, a percentage much lower

than it was ten or fifteen years ago. In addition, a considerable proportion of the special shapes are made by the soft-mud process. A hand molder and a boy can mold approximately



(a)

FIG. 95.—Method of hand molding shapes. (a) Building up the “walk”; (b) forming the sides; (c) forming the ends; (d) throwing the “walk” into the mold; (e) the “walk” thrown on the mold; (f) bumping; (g) cutting off the cap; (h) slicking; (i) placing on the hot floor; (j) stripping mold; (k) removing loose pieces, (l) assembling mold. (Courtesy of A. P. Green Fire Brick Company.)



(b)

400 standard bricks per hour, and a hand represser and two off-bearers can handle up to 550 bricks per hour, a rate that demands very skillful operation of the repress. In hand molding special shapes from soft mud, a molder and helper will turn out about seventy-five 9-in. equivalents per hour.

(c)



(d)

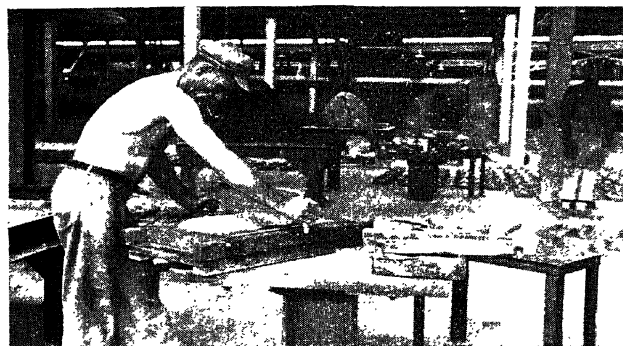


(e)





(f)



(g)

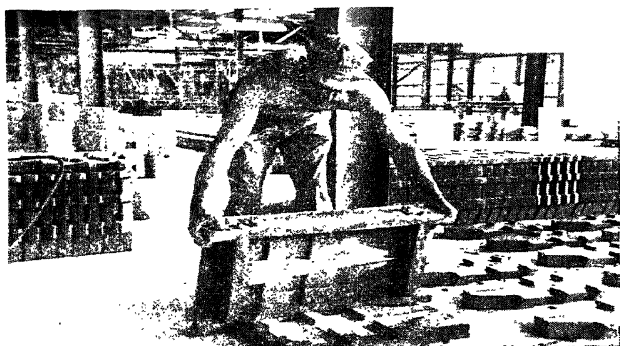


(h)

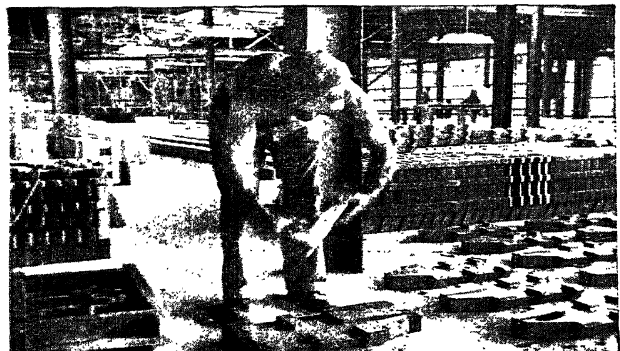
(i)



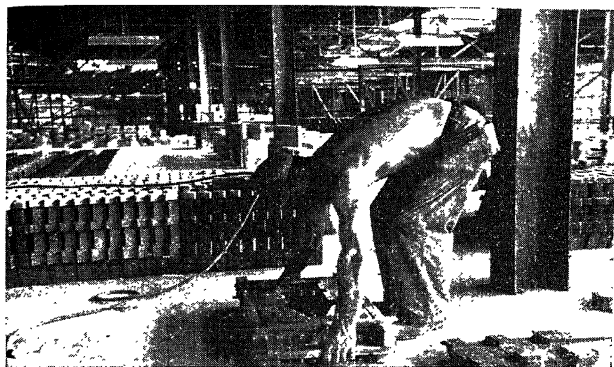
(j)



(k)



It should be recalled that in the soft-mud process, the clay contains an amount of water somewhere between the critical point and the saturation point, which allows the plastic mass



(1)

to be deformed with a comparatively small force without rupture and yet permits it to have a sufficiently high yield value to prevent the shape from slumping after it is removed from the

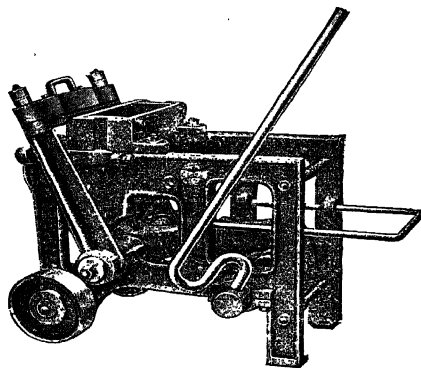


FIG. 96.—A hand re-press. (Courtesy of International Clay Machinery Company.)

mold. However, the yield value is only slightly above the gravity forces, as any shock or jar on the freshly molded shape will make it deform.

The handmade brick are of open structure, quite resistant to spalling, and easily cut by the bricklayer.

Silica brick are usually made by the soft-mud process. The ganister is given a short treatment in a wet pan, when about 2 per cent milk of lime is added. The comparatively nonplastic mix is thrown into molds in the same way as for hand-molded

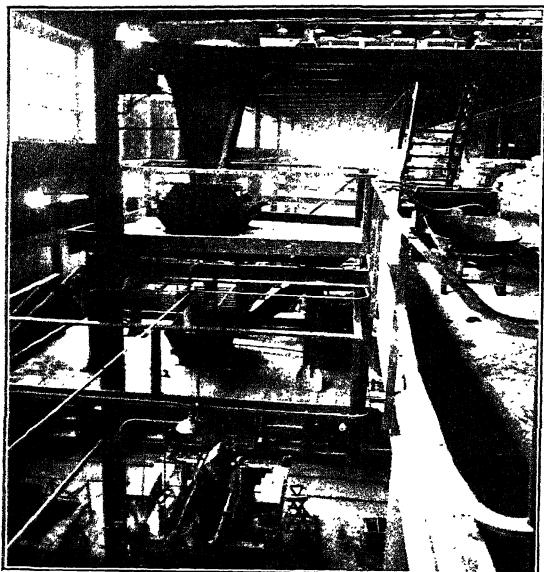


FIG. 97.—A machine for molding silica bricks. The mud is dropped from the upper hopper into the mold below. (Courtesy of Harbison-Walker Refractories Company.)

clay bricks. However, the molds are steel, and push blocks have to be used in stripping because of the low strength of the brick. Since the yield point of the mix is very low, care must be taken not to jar the finished piece until it becomes dry.

Machines are now used for molding silica brick. The hydraulic press is used to some extent, but a dropping machine⁽⁶⁶⁾ that simulates hand molding has been quite successful in this country. It (Fig. 97) is entirely automatic, dropping slugs of the silica mix into the mold on a heavy anvil, slicking, and stripping.

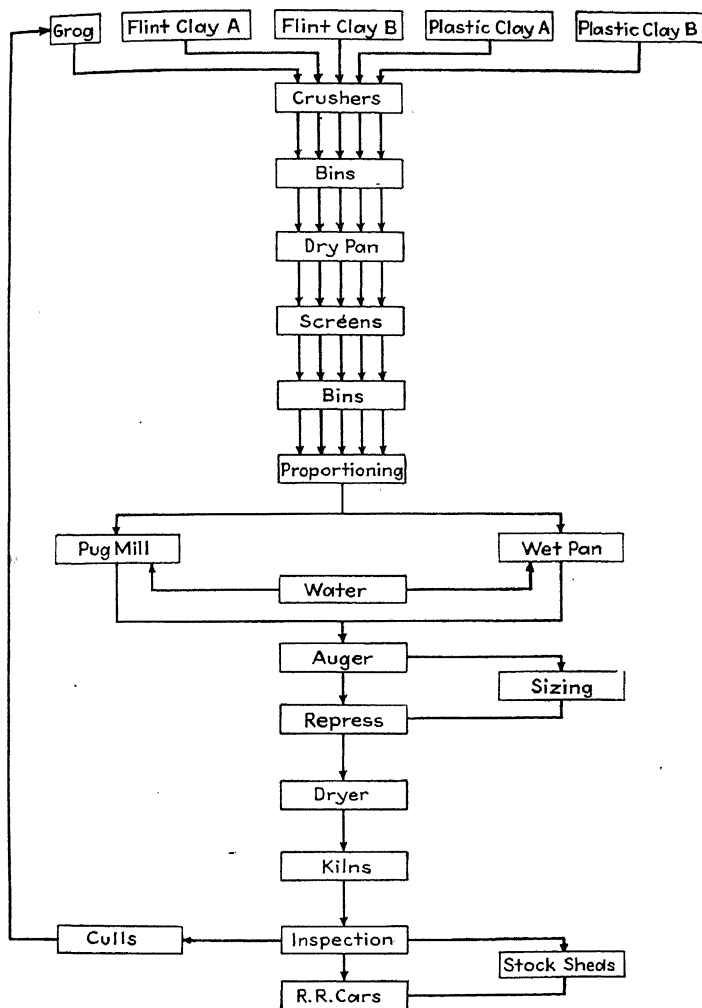


Fig. 98.—A typical flow diagram for the manufacture of stiff-mud brick. (Courtesy of E. H. Van Schoick, American Refractories Institute.)

✓ 4. **The Stiff-mud Process.**—The stiff-mud brick are made with a consistency just above the critical point; therefore considerable force is required to form the clay. Most of the refractories made by this process are formed by forcing the plastic material through a die from which it emerges as a more or less homogeneous column that can be cut off into definite lengths. This column is generally produced by an auger, consisting of a propeller-shaped screw running in a trough, which forces the clay with high pressure through a die. Steam-pressed brick are forced through a die with a piston operated by steam pressure, an intermittent process.

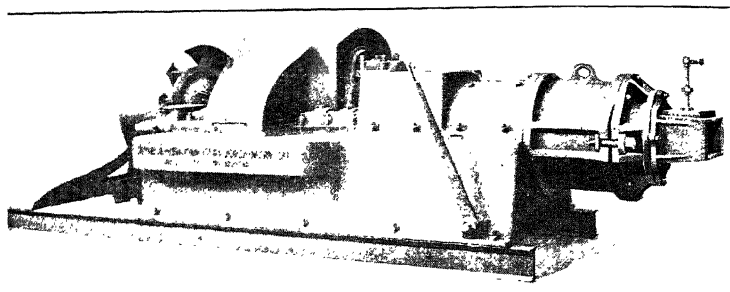


FIG. 99.—An auger for producing a uniform column of clay. (Courtesy of W. A. Riddell Company.)

A flow sheet of the stiff-mud process is shown in Fig. 98, in which the clays are prepared in much the same way as for the handmade bricks. Water is added to the mixture with either a wet pan or a pug mill. The latter is generally preferred because it is a continuous process and better adapted to feeding the auger. The pug mill (Figs. 93 and 94) is a long, trough-shaped container with one or two horizontal shafts running down the center, having attached to them suitable blades for kneading and mixing the clay and propelling it gradually toward the exit end. Water can be added to the material in the pug mill to bring the mixture to the proper consistency.

The auger, as shown in Fig. 99, must be a well-designed machine in order to produce a uniform column. It is important in designing the die to assure an even velocity of the clay in all parts of the stream to prevent strains. Also the auger must be

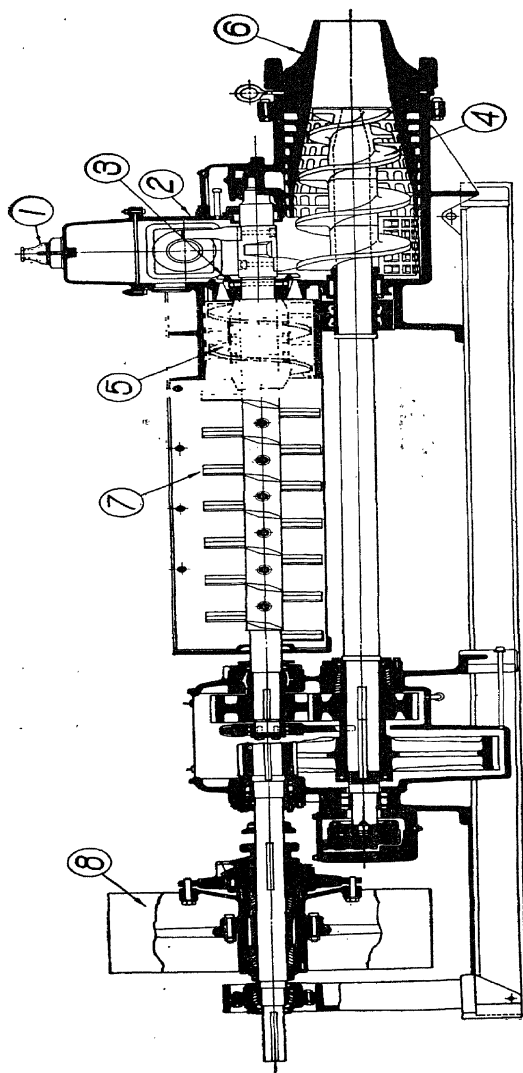


FIG. 100.—Section of deairing auger. (Courtesy of The Falc-Root-Heath Company.)

designed so as to prevent laminations, which often occur in the center of the column as an S-shape crack. The die itself is generally lubricated with oil to reduce the friction, and often it is steam heated for the same purpose. It has been found that if the clay is mixed in the auger in a vacuum chamber,^(71,73,76) the air is readily removed and a more dense and homogeneous column is produced in passing through the die. One method of deairing in the auger is shown in Fig. 100. Deairing has become

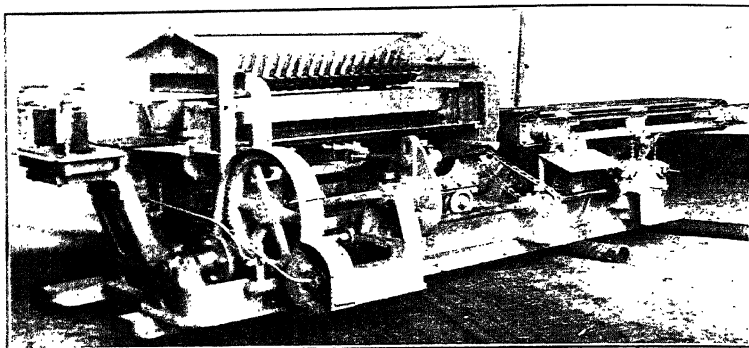


FIG. 101.—A multiple-wire cutter for dividing the column of clay from the auger into bricks. (Courtesy of The Bonnot Company.)

a very common practice in stiff-mud operation in the last few years and enables the production of sound bricks from clays that previously could not be readily handled. It also permits a denser structure to be obtained. However, deairing is not necessary for all bodies, as many of them can be handled quite satisfactorily without it. In fact, deairing seems to make some plastic mixes harder to dry and burn.

The column of clay from the auger is cut into uniform sections with a wire cutter, as shown in Fig. 101. Many designs of cutter are available, but they all operate on the principle of passing one or more steel wires through the column. It is difficult to operate a wire cutter satisfactorily if the grog content of the body is very high or if the size of the grog is very large.

There are few cases where the wire-cut brick produced are sufficiently uniform in size for use as refractories. Therefore the general practice is to pass them through a machine re-press

as shown in Fig. 102, where they are actually formed to size and the brand put on. After being re-pressed, the brick are quite firm and can be readily handled and stacked on the drier cars.

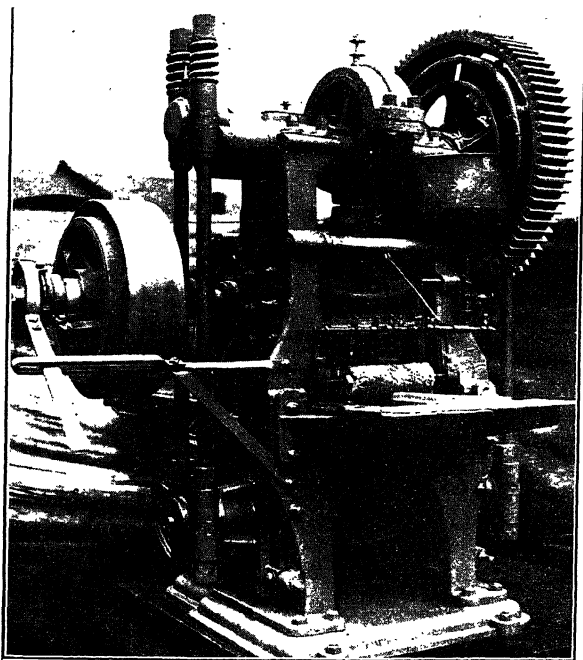


FIG. 102.—A machine re-press. (Courtesy of The Bonnot Company.)

Since stiff-mud brick have a strong tough structure, are good bricks for cutting, and are quite resistant to abrasion and slag, they would be used wherever a dense, strong brick is needed.

It is estimated that approximately 22 per cent of the fireclay refractories made in this country are produced by the auger and re-press. Inasmuch as an auger will produce as many as 6,000 bricks an hour and one machine re-press will turn out from 1,500 to 2,200 bricks per hour, four re-presses are generally set up with one auger.

(a)

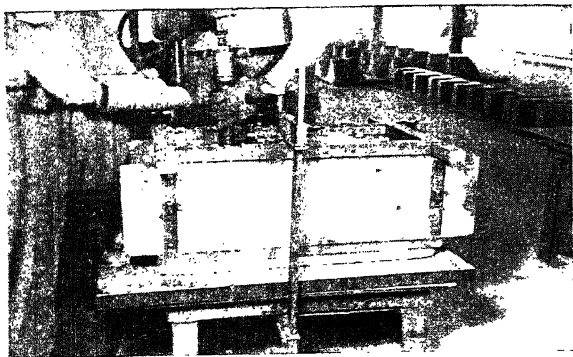
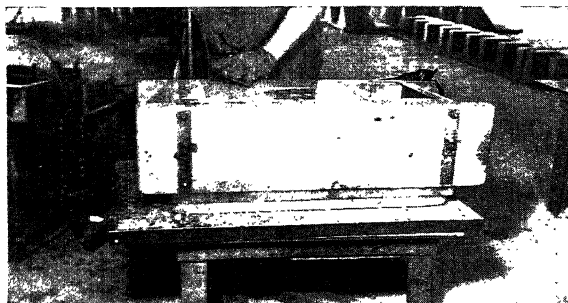
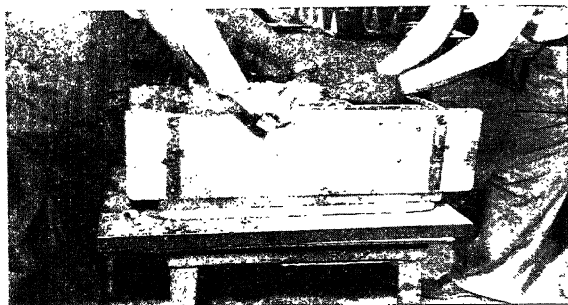
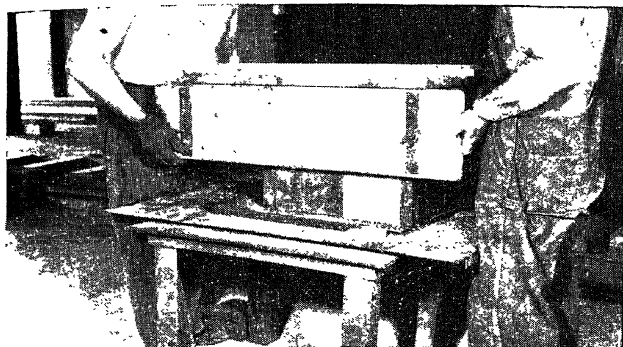
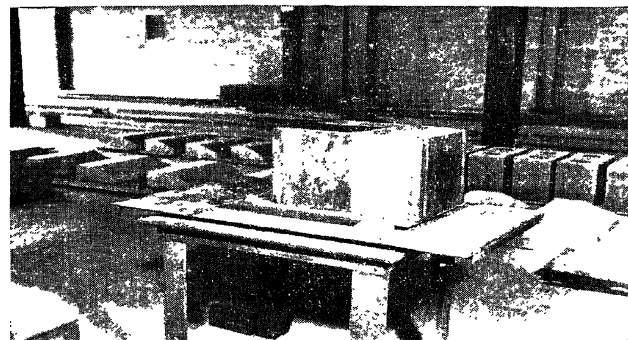


FIG. 103.—Method of air ramming of stiff-mud shapes. (a) Ramming (note continuous feeding); (b) cutting off top; (c) slicking; (d) stripping; (e) showing loose pieces; (f) finished block. (Courtesy of A. P. Green Fire Brick Company.)

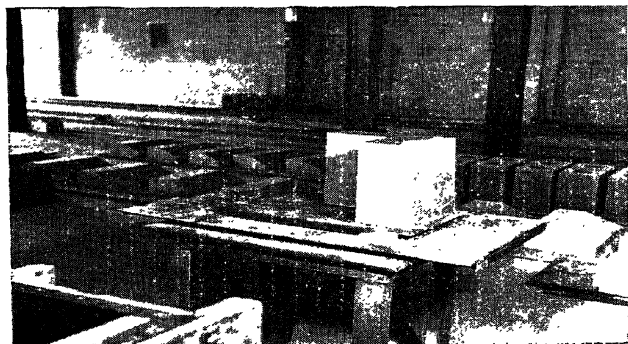




(d)



(e)



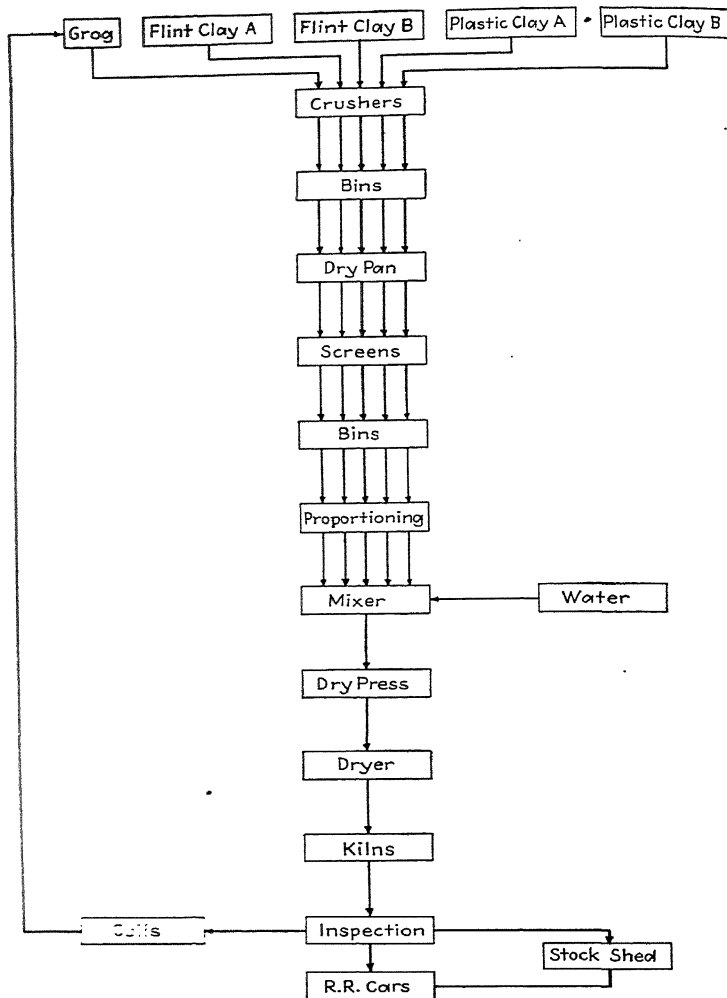


FIG. 104.—Typical flow diagram for the manufacture of dry-press refractories.
(Courtesy of A. C. Hughes, American Refractories Institute.)

A good many shapes, especially the medium and large ones, are made with a stiff-mud mix containing a high grog content because of the small total shrinkage and low warpage, even though the labor cost is higher than for the soft-mud method. Hard maple molds lined with $\frac{1}{16}$ -in. steel are generally used, often with loose pieces. The mix is fed in slowly and continuously by one man while the other consolidates it with an air

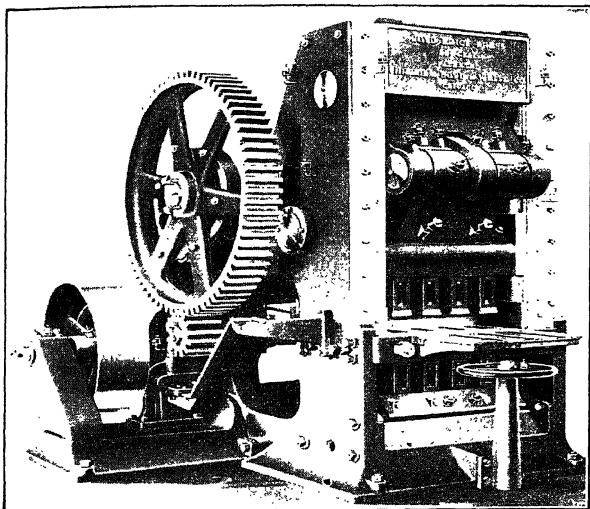


Fig. 105.—A dry press for forming bricks. (Courtesy of Chisholm, Boyd and White Company.)

hammer having a corrugated foot. The whole process is clearly shown in the photographs of Fig. 103.

5. The Dry-press Process.—In the dry-press process of making refractories, the clay has the consistency of a damp powder containing perhaps 7 to 10 per cent water. Only by high pressure can it be consolidated into a homogeneous mass. The flow sheet for the dry-press process is shown in Fig. 104, in which the preparation of the clays is very much the same as for the preceding processes. In the Missouri district, the clays and grogs are often coarsely crushed, stored in bins, and recombined by feeders into dry pans where they are further ground, screened,

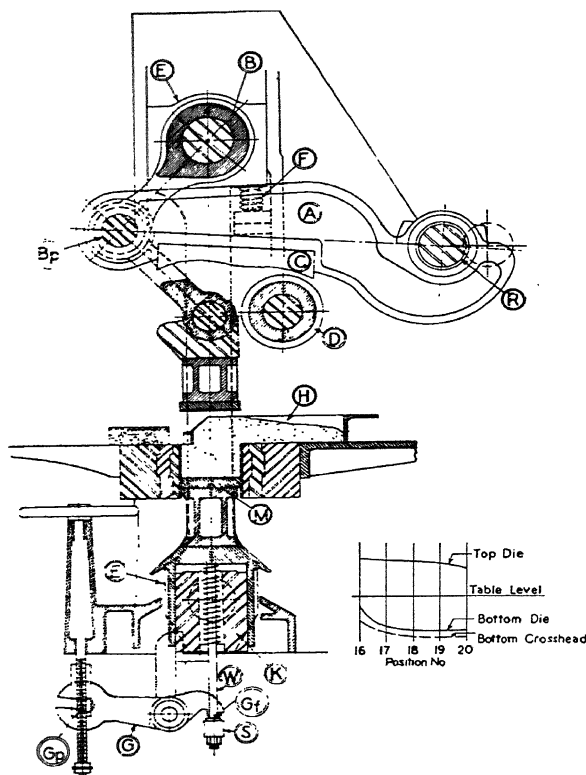


FIG. 106a.—This figure shows the various cycles in the operation of a dry press when forming a brick. (a) Represents position No. 18. The crankshaft *R* has reached position No. 18 and has moved connecting beam *A* to its most forward position. The toggle pin *B* and connecting beam have now entered the portion of the cycle where they follow the radius of upper toggle *B* to position No. 2, where the lifting shoe *C* again comes in contact with lifting roller *D*. The side bars *E* have traveled from their topmost point at position No. 13, to their lowest point at No. 18, compressing equalizing spring *F* and bringing with them the upper toggle *B*, the lower crosshead *K*, and the pressure-adjusting mechanism. They pivot at point *G_p*, cause point *G_f* to press on saddle bar *S* and, by the tension placed on saddle rod *W*, they bring the lower die *M* to a level predetermined by the setting of point *G_p*. The charger *H* remains at rest until position No. 14, at No. 18 it has removed the finished brick and has begun to return to rest after it has filled the mold boxes. (Prepared by Dr. G. E. Seil, E. J. Lavino and Company.)

and tempered. The mix is aged for 24 hr. and then fed to the presses. Modern practice seems to be favoring the more careful

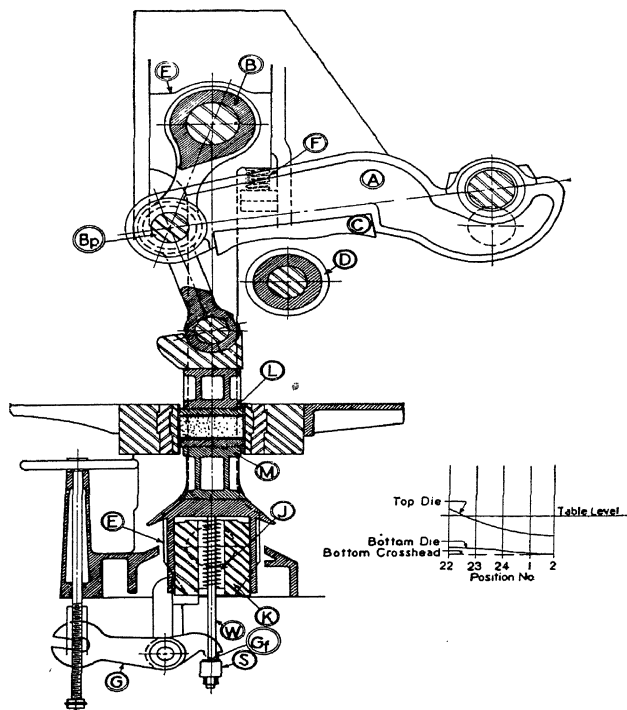


FIG. 106b.—Represents position No. 24. At position No. 24 the connecting beam *A* and the upper toggle pin *B_p* are about midway along the arc made by the upper toggle *B*. The lifting shoe *C* has not yet come in contact with the lifting roller *D*. The side bars *E*, the upper toggle *B*, the lower crosshead *K*, and the pressure-adjusting mechanism *G* remain in the same position as No. 18. The upper die *L* has moved from its peak position at No. 16 to No. 24, where it has come in contact with the loose material and has slightly compressed it. The lower die *M*, which had been stationary from No. 18 to No. 23, has now moved to a new level owing to the pressure of the upper die on the now partly pressed material. This action compresses saddle springs *J*, lowers saddle rod *W*, and saddle bar *S* from point *G_r* on the pressure-adjusting mechanism. The equalizing spring *F* remains as before. The charger *H* has returned to rest at No. 20.

control of the sizing of the grog and flint clays by screening and recombining in definite proportions. The mixture of dry

materials is then moistened in a pan or a pug mill and brought up to the proper consistency. Certain types of special mixers⁽⁹²⁾ are used to a considerable extent for this purpose. The mixed

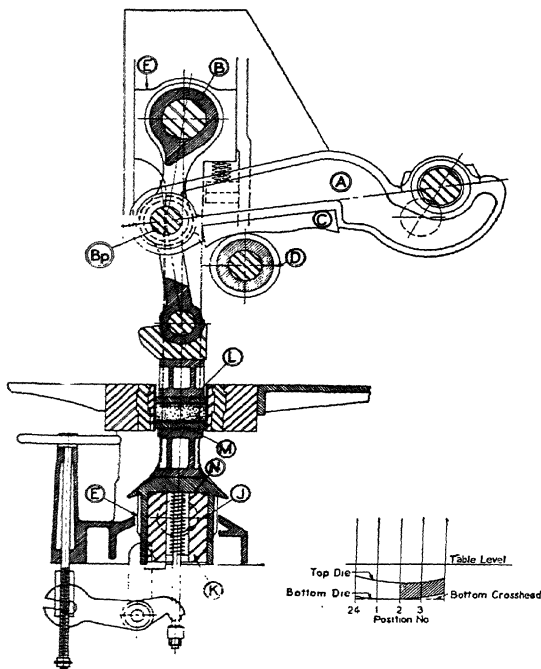


FIG. 106c.—Represents position No. 2. At position No. 2 the upper toggle pin B_p and connecting beam A have completed the movement along the radius of upper toggle B , and have now brought the lifting shoe C in contact with lifting roller D . The side bars E remain in the same position as shown in Figs. No. a and No. b . The upper die L has further compressed the material, but has not yet pressed the brick to its finished size. The pressure of the top die on the material has caused the lower die M to compress fully the saddle springs J to where the saddle plate N comes in contact with the lower crosshead K .

material is delivered to a hopper over the dry press, where the mixing action is continued, and permitted to flow into the dry press as needed.

The dry press itself (Fig. 105) is usually the toggle type, pressing four standard bricks at one time. However, hydraulic

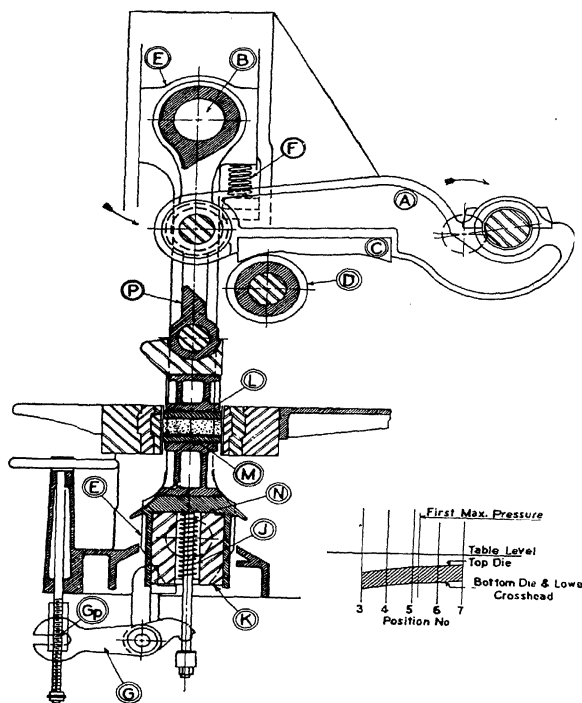


Fig. 106d.—Represents position No. 5- $\frac{1}{4}$. At position No. 5- $\frac{1}{4}$ the first maximum pressure is reached and the material is pressed to its finished thickness. The side bars *E*, the upper toggle *B*, the lower toggle *P*, the upper die *L*, and lower die *M*, and lower crosshead *K* have continued to rise owing to the action of the connecting beam *A* and lifting shoe *C* on lifting roller *D*. At this point the side bars have lost contact with equalizing spring *F*, saddle plate *N* is still in contact with lower crosshead *K*, while saddle springs *J* are still fully compressed. The pressure-adjusting mechanism *G* has been rising with the lower crosshead using point *G_p* as a pivot.

presses are used for certain types of refractory. The operation of the toggle press will be shown clearly by the excellent diagrams, prepared by Dr. G. E. Seil, in Fig. 106, which shows the various

cycles in the pressing process. In order to make uniform brick, it is essential that the mix be uniform, that the same weight of the material be always charged into the dies each stroke, and that it be evenly distributed in the die box.^(81,82,91) For non-

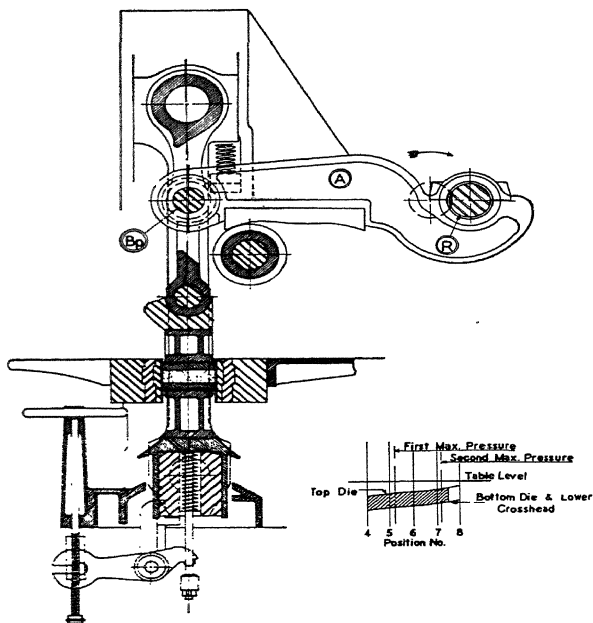


FIG. 106c.—Represents position No. 6. Conditions at position No. 6 are changed slightly. The side bars have risen a little higher and the crankshaft *R* has reached its maximum throw, bringing connecting beam *A* to its extreme horizontal movement and toggle pin *B_p* over the center line of the side bars.

plastic mixes⁽⁸⁵⁾ like magnesite and chromite, a small amount, about $\frac{1}{4}$ of 1 per cent, of organic binder such as dextrine is used.

Until recently, the exact pressures in the toggle press were not known precisely. Now^(81,82) they can be determined by the stretch of the side arms, which indicate pressures as high as 14,000 lb. per sq. in. With many materials, the maximum pressure is limited by the expansion, which causes pressure crack-

ing, of the entrapped air on releasing the pressure. Recently, many presses⁽⁸⁴⁾ have been fitted with vacuum attachments that pull the air out of the die box and mix as soon as the top pad enters the box. Slots about 0.007 in. wide in the pads connect to the vacuum system.

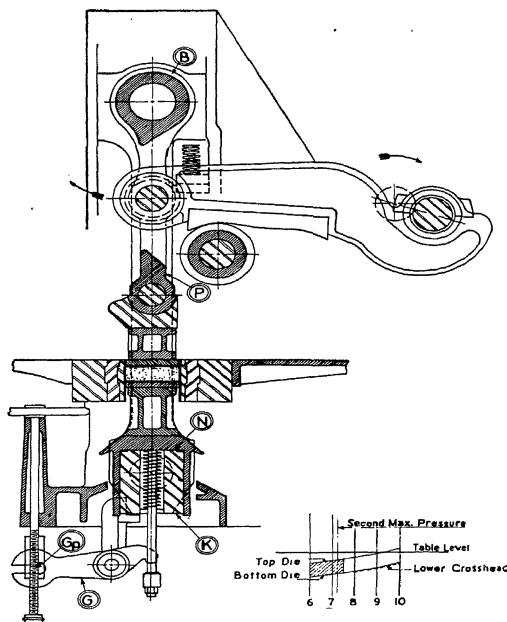


Fig. 106f.—Represents position No. 7- $\frac{1}{4}$. At position No. 7- $\frac{1}{4}$ maximum pressure is again developed as upper toggle *B* and lower toggle *P* again pass over the center line of the side bars. The saddle plate *N* is still on contact with the lower crosshead *K*, where it will remain until No. 8 is reached. The pressure-adjusting mechanism *G* is still rising with the side bars *E* and lower crosshead, using *G_p* as a pivot.

The brick discharged from the dry press can usually be set on the tunnel kiln cars with little or no drying. The rate of forming dry-press brick on the toggle press runs between 1,000 and 2,000 brick per hour. The dry-press process is used very extensively in the industry, and it is estimated that 70 per cent

of the fireclay refractories and practically all the magnesite and chrome refractories are made by the dry-press process.

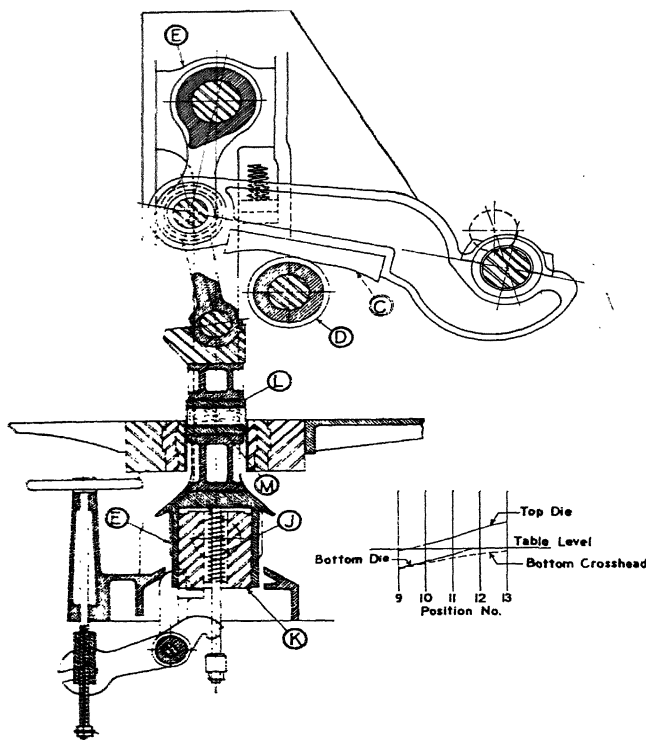


FIG. 106g.—Represents position No. 11. At position No. 11 the side bars *E* have almost reached their highest point. The saddle springs *J* have come into action and have begun to push the lower die *M* to table level removing the finished brick. The upper die *L* has been rising slightly faster than the lower crosshead *K*. The brick is held against its face by the pressure of the saddle springs. The lifting shoe *C* is still in contact with the lifting roller *D*.

The bricks produced by dry pressing are very uniform in size, with strong corners and edges and little tendency to warp. They have good spalling resistance and generally good resistance to load.

Mixes of the dry-press consistency can be molded by hand ramming under special conditions. Patented processes make a deflocculated slip of clays^(80,83,87) and then mull in carefully

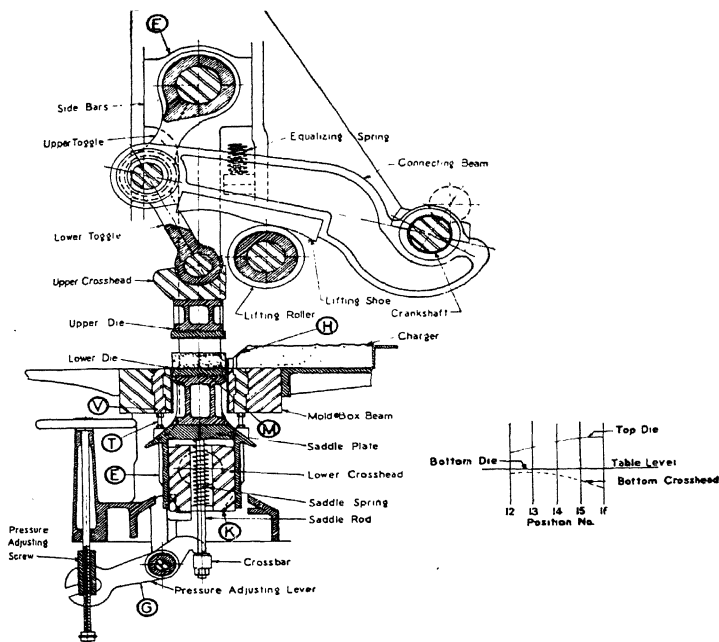


FIG. 106h.—Represents position No. 14. The crosshead *K* at No. 14 has passed its highest point. The lower die *M* has been raised to table level where it is stopped by bolts *T* striking mold-box beams *V*. The charger *H* at this point has begun to remove the finished brick. The downward motion of the side bars *E* and crosshead *K* has lowered the pressure-adjusting mechanism *G*.

sized grog. The resultant mix contains about 90 per cent grog and 10 per cent clay, with a total water content of 5 to 6 per cent. By heavy ramming in rigid steel molds, large shapes can be made with a total shrinkage of not more than $\frac{1}{4}$ of 1 per cent. The photographs in Fig. 107 show clearly how a large tile is made by this process.

6. **Molding of Insulating Firebrick.**—The production of highly porous, lightweight refractories requires somewhat different methods from that employed for the heavier materials. Therefore, it was thought advisable to devote a special section to the

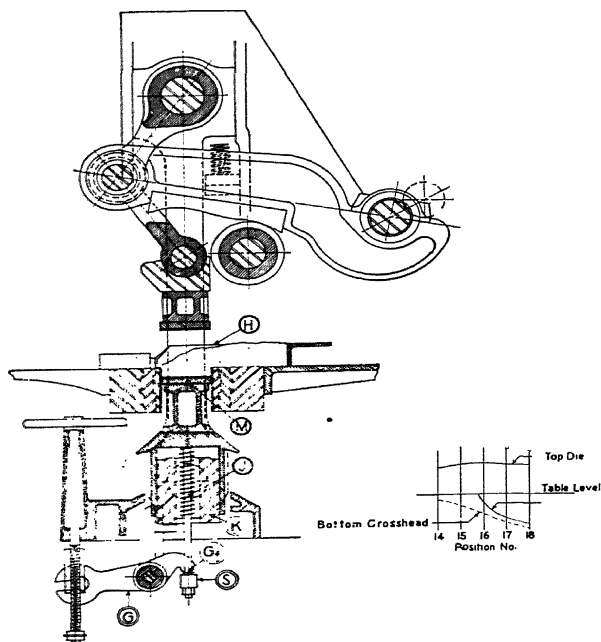
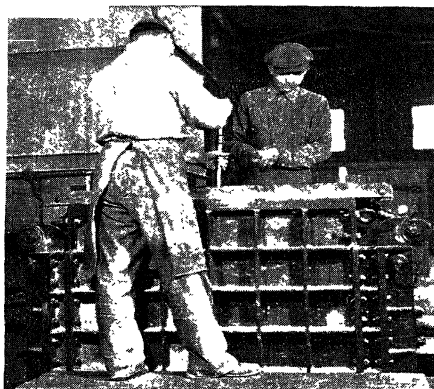


FIG. 1066.—Represents position No. 16. At position No. 16 the crosshead *K* has continued to move downward taking with it the pressure-adjusting mechanism *G* until point *G₂* comes in contact with saddle bar *S* and starts to compress saddle springs *J*. The setting of the pressure-adjusting mechanism decides the length of movement of the lower die *M* and allows the mold box to be filled to the desired depth. The charger *H* has further removed the finished brick and has started to fill the mold with loose material.

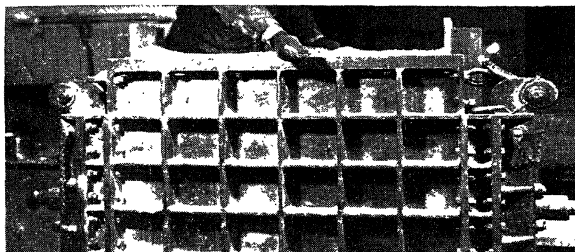
molding of this product. An excellent review of this subject is given by Foster.^{93a)}

Method of Obtaining Pores.—Perhaps the most common method of producing pores in a fireclay product is to introduce in the plastic mix an organic material that later on can be burned out

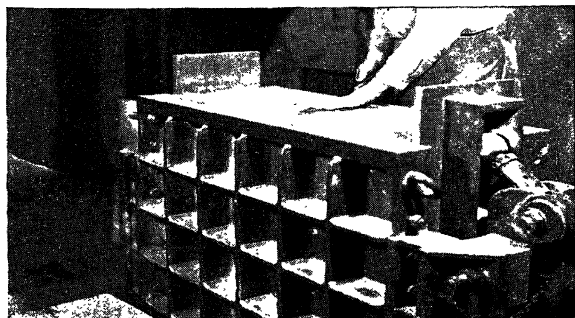


(a)

FIG. 107.—Making a large tile with a low water-content mix. (a) Air ramming; (b) cutting off the top. (c) finishing the top; (d) finished block; (e) removing the mold; (f) block ready for drying. (Courtesy of A. P. Green Fire Brick Company.)

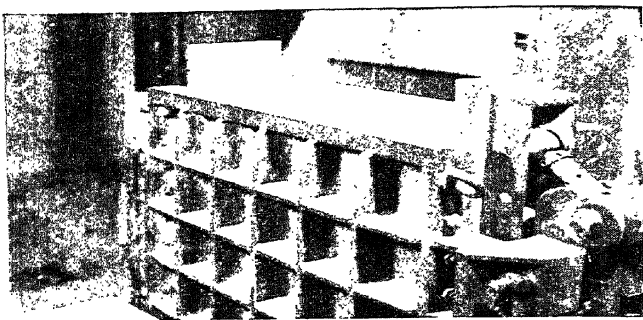


(b)

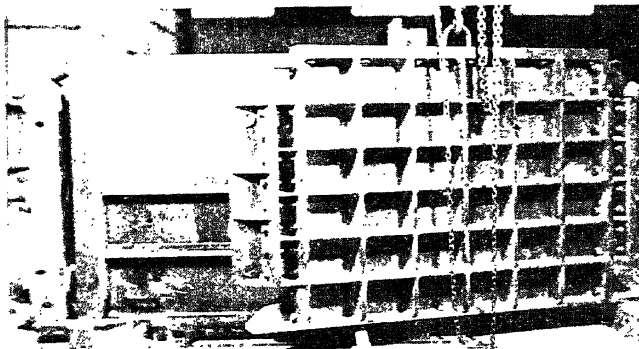


(c)

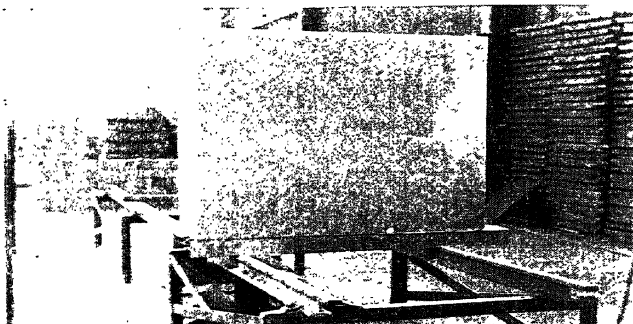
(d)



(e)



(f)



to leave voids. Sometimes this organic material may be peat, which is naturally mixed with the fireclay, but usually it is necessary to add granular organic material such as ground wood, cork, or other materials of this type. Of course, the properties of the finished product will depend not only on the clay but on the size, shape, and amount of the organic particles.

A somewhat different method of producing pores consists in adding to the clay mix granular sublimable material such as flake naphthalene.^(93b) On drying the ware at high temperature, the naphthalene can be sublimed, leaving pores in the dried-clay product. The naphthalene vapor can be cooled and used over again. Although this process has been employed industrially, it is not in common use at the present time.

Still another method of forming the pores in the clayware is to introduce into the clay, which has been made to the consistency of a thick slip, bubbles of gas that are sufficiently stable to remain in the mix until the material is dried and burned. This method seems very attractive, as the cost of the organic material is eliminated; but practically, difficulties are encountered in stabilizing the bubbles so that they are of uniform fine size and evenly distributed throughout the mass. The method patented by Eriksson^(93c) produces bubbles in the clay mix by the addition of powdered aluminum or zinc and alkali so that each particle of aluminum is decomposed and forms a bubble of hydrogen. Others accomplish the same effect by stirring finely divided lime into the soft mix and then acidifying, with the result that each particle of lime is decomposed, forming a bubble of carbon dioxide. Still another method, such as those patented by Ericson^(93d) and Roos,^(93e) consists in making a pre-formed foam which is then stirred into the clay slip. Such a foam, of course, has to have considerable stability in order that this process may be successful.

All the bubble-structure refractories must have some stabilizing device to hold the bubbles as individuals and prevent their coalescing into larger ones. In the Husain and Bole^(93f) patents, this is accomplished by adding gypsum plaster to the mix and permitting it to set, thus stabilizing the bubbles. In fact, there is probably no successful bubble process that does not use some stabilizing method, either plaster or a flocculent;^(93g) and for this reason, it is difficult, because of the fluxing elements added,

to make high-temperature insulating firebrick by the bubble process.

A high porosity can also be obtained by adding to the mix an inorganic refractory material having itself a high porosity. Such materials include diatomaceous earth, bloated clay pellets, or porous grog.

Molding Methods.—The molding of the insulating firebrick mixes is not particularly difficult, as the mixtures containing organic matter can be readily molded by the soft-mud method, whereas the bubble method is best carried out by pouring the slip into molds until the mass has set. As far as it is known, no successful results have been obtained by using the stiff-mud or dry-press method for these highly porous materials; for if they contain organic matter, they are usually rather elastic and difficulties from pressure cracking are troublesome. On the other hand, if the bubble process is used, any considerable amount of pressure would squeeze the air out of the structure and the density would be too high.

TABLE 33.—USE OF WEAR-RESISTING METALS

	Pug knives	Auger dies	Muller tires	Dry- press pads	Dry- press liners
"Ni-hard".....	×				
High-chrome steel.....				×	
White cast iron.....	×		×		
Tool steel.....				×	×
Stellited steel.....				×	×
Tungsten carbide.....					
Chrome moly steel (heat-treated)			×		

7. Abrasion-resisting Metals.—In the stiff-mud and dry-press process previously mentioned, numerous metal parts received considerable wear as a result of the abrasive action of the grog particles in the mix. These parts include the mullers of the wet and dry pan, the blades of pug mills and augers, auger dies, and the die boxes of re-presses and dry presses. Table 33 will give a summary of a number of wear-resisting metals that have been used.^(70a) There is, however, at present no great uniformity in the use of these materials, as some plants will obtain better life with one and some plants with another, owing, perhaps, to

the differences in their mixes. A great deal of development work is still to be done in this field.

Dry-press and re-press die wear depends greatly on the mix. One hundred million bricks can be produced from plastic and flint clay in a set of liners; but when high-grog clay bricks or highly burned magnesite or chrome are used, the life may drop to as low as 5,000 bricks.

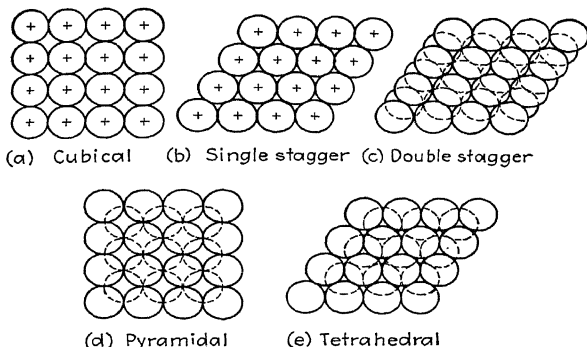


FIG. 108.—Various methods of packing spherical particles.

8. Grog Sizing.—The manufacturer of refractories is coming more and more to realize the importance of maintaining consistency of particle sizes of the grog or flint clay portion of his mix, especially where he has to make a low-porosity or low-shrinking refractory or an unburned refractory with a chemical bond. It has also been found that proper sizing helps the spalling resistance. Some manufacturers are going so far as to divide their particles by screens into a series of size fractions and then are recombining them by definite weights to produce the desired distribution. Others control size by proper adjustments of screens and crushers.

If the one-component system is considered first, *i.e.*, particles having a single diameter, it will be found that the closeness of packing depends on the arrangement of particles and their shapes. Taking the simplest case, *i.e.*, spheres, there are five different methods of packing,⁽¹⁰⁹⁾ which are shown in Fig. 108 and the results given in Table 34.

In the case of irregular particles as would be obtained from a crusher, the packing varies between 40 and 50 per cent, although theoretically, with perfectly arranged cubes, the voids would be zero.

TABLE 34.—VOIDS WITH DIFFERENT METHODS OF PACKING⁽¹⁰⁹⁾

Type of packing of spheres	Voids, per cent	Fig. No.
Cubical.....	47.64	108a
Single stagger (cubical tetrahedral).....	39.55	108b
Double stagger.....	30.20	108c
Pyramidal.....	25.95	108d
Tetrahedral.....	25.95	108e

Consider next, the two-component system wherein a coarse grain and a fine grain are mixed and shaken down to the minimum volume; the clearest picture of the situation can be obtained by referring to the packing diagram of Westman,^(95,107) shown in Fig. 109. Along the base is plotted the proportion of coarse

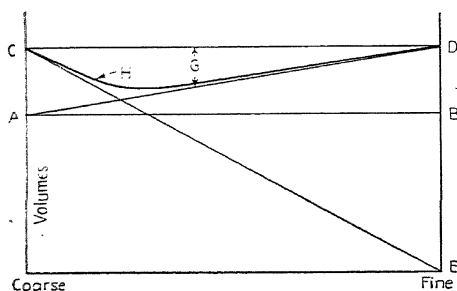


FIG. 109.—Packing diagram for two sizes of particles.

and fine in the mix, giving a constant total weight. On the vertical scale are plotted volumes. A line *AB* represents the true volume of the mixture. Point *C* represents the apparent volume of the coarse mix, and *D* the apparent volume of the fine mix, the apparent volume being the true volume plus the volume of voids. Now suppose that a small proportion of the coarse material is replaced by fine material. It is obvious that

up to a certain point, the fines will simply fill the voids between the larger grains and therefore the total apparent volume will decrease in proportion to the amount of fines added. Accordingly, the theoretical apparent volume will follow the curve *CE*. Now starting from the other end of the diagram, if a certain amount of the fine material is replaced by the coarse, the coarse material will displace an equal volume of fine material and the voids existing in the fines. Therefore the total volume will decrease owing to an elimination of a portion of the voids in the finer material. Consequently, the line *AD* will represent the theoretical apparent volumes. Where the lines *CE* and *AD* cross will be the minimum volume from a mixture of coarse and

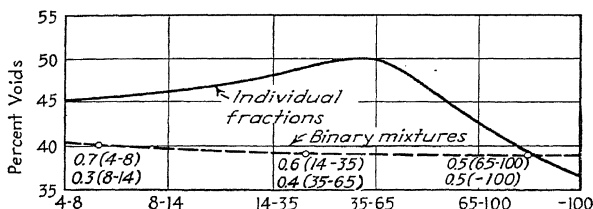


FIG. 110.—Porosity diagram for crushed kaolin grog; individual fractions and binary mixtures. (*J. Am. Ceram. Soc.*)

fine having an infinite ratio between the diameters. Actually, however, we have a finite ratio, and the actual curve of apparent volume will be indicated by *H*. The line *CD* is the apparent volume of the fractions before mixing, and the distance *G* represents the shrinkage in volume during the mixing process.

Results obtained on crushed kaolin grog are given in Fig. 110, where are shown individual screened fractions and binary mixtures of these fractions mixed to give the densest packing.

When we come to systems of three components, the apparent volume can be indicated by surfaces. It will be found, however, that from practical considerations, little is gained by using more than two or three components in the mixture because of the impossibility of getting large-diameter ratios between the successive sizes. Figure 111 shows a three-component diagram for the crushed kaolin grog of Fig. 110. The densest mix has a proportion of 40 per cent fine, 50 per cent coarse, and 10 per cent medium, giving a porosity of 22 per cent. ✓

/ Chemical Bonding.—A great deal of interest has been shown recently in refractories that are chemically bonded with a setting material, which gives to the brick sufficient mechanical strength so that it can be used in the furnace without previous burning. In order to do this, it is necessary to have a large proportion of well-fired nonplastic material in the brick and have it sized in such a way as to give a very dense packing. In addition, the bricks must be pressed under high enough pressure to reduce the

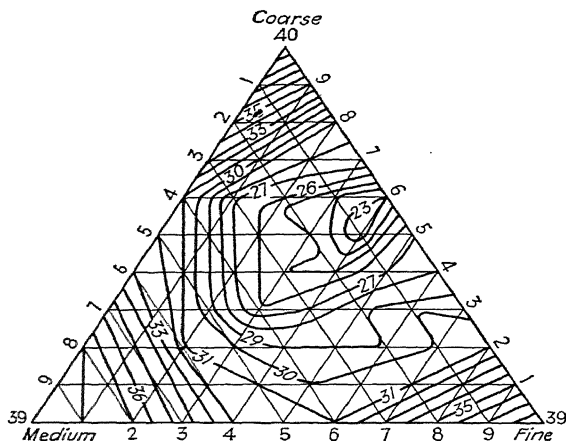


FIG. 111.—Porosity diagram for crushed kaolin grog; ternary mixtures. (*J. Am. Ceram. Soc.*)

voids as far as possible. Bricks of this type have been made of magnesite, chrome, and fireclays.

One type of bond consists of magnesium chloride or magnesium oxychloride, used generally with a magnesite or chrome base. The patent of France^(112,113) is typical of this type. Another bond is phosphoric acid, which has been used with a zirconia base according to the patent of Morgan^(119,125) and with an aluminous material in the patent of Hood.⁽¹²¹⁾ Bonds have also been suggested, such as silicate of soda⁽¹¹⁷⁾ and a soluble aluminum salt, according to the patent of Betts.⁽¹¹⁵⁾ However, one difficulty with the use of soluble salts is their migration to the surface on drying.

A great many organic types of bonds have been suggested. A synthetic resin bond is indicated in the patent of Danehower,⁽¹¹⁴⁾ and Schwartzwalder⁽¹²⁴⁾ suggests the use of bakelite. Aluminum formate is used for bonding silica-alumina materials by Rohde.⁽¹²⁸⁾ Methyl silicate has also been suggested in a number of occasions as a bond for silica-alumina refractories, since a colloidal silica having considerable strength is precipitated. Other organic materials such as linseed oil and sulfide waste liquor^(126,127) have been suggested. For lower temperature refractories, it is possible to use a high-alumina cement.

In looking over the list of bonds, it will be noted that many of them are at present too expensive for use anywhere except in laboratory-type refractories. Others have some practical difficulties; *e.g.*, the phosphoric acid is so hygroscopic and so hazardous to the health of workmen that it has operating difficulties. Probably the most useful bonds at present are the magnesium oxychloride, sulfate waste, and high-alumina cement.

The chemically bonded refractories in some types of service give results superior to the burned refractories, especially in resistance to spalling; consequently, they have definitely taken a place in our refractory production. Of course, the first thought on considering this type of refractory is the great saving in firing cost; but when the problem is analyzed, it is usually found that with the additional cost of the bond and the necessity for carefully sizing the nonplastic, which comprises practically the whole brick, the total cost is little, if any, less than for burning the brick.

10. Hot Molding.—The suggestion has been put forth from time to time of producing refractories by pressing the heated refractory material in the mold so that the bonding would take place by welding together the particles while they were sufficiently hot to have a certain amount of glass in the viscous condition. Such a method is suggested in the patent of Duffield.⁽¹²⁹⁾ Many experimenters have shown that a comparatively strong brick can be made at a temperature much below the burning temperature if pressure is exerted. However, this attractive process of molding refractories has not proved commercially successful because of the great difficulty in providing molds that will operate at the high temperatures necessary and still give a reasonable amount of life.

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CHAPTER VIII

DRYING

1. **The Mechanism of Drying.**—The work of Sherwood^(4,5,8) and his collaborators has done much to give a clear picture of the drying process in porous solids. It is logical to divide the drying into two periods; the constant-rate period and the falling-rate

The Constant-rate Period.—At the start of the drying process, when the clay contains enough water at least to fill the pores, there will be a continuous film of water over the surface particles, as evidenced by the comparatively dark color of the wet clay. It is therefore not unexpected to find that the rate of drying per unit area of surface is substantially the same as for a free water surface. This rate in terms of temperature, humidity, and velocity of the air is shown in Fig. 112. As the drying proceeds at this rate, it is obvious that water must travel through the pores toward the surface to supply the evaporation loss. In all but exceptional cases, where the drying rate is very high or the clay very fine grained, the water will travel by capillary forces as fast as it is carried away. In the case of clay, the piece will shrink in volume equivalent to the volume of water lost until the particles touch, and thereafter air must enter the pores to take the place of the water. Soon after this happens, it will be found that the water cannot travel to the surface fast enough to maintain an unbroken surface film; so the drying rate starts to decrease. This rather sharply defined point may be called the "critical point" and corresponds approximately to cessation of shrinkage.

It might be thought that a nonshrinking material like sand and water would not show any constant-rate period because the pores would start to empty at once. Experiments show this to be true when the particles are fine; but when the particles are coarse, the resistance to flow is so slight that even with air in the pores, the surface drying rate is the governing factor. This is shown clearly in Fig. 113 for a fine and coarse sand.

The Falling-rate Period.—Beyond the critical point, the drying rate is governed by the rate of transfer of water from the interior

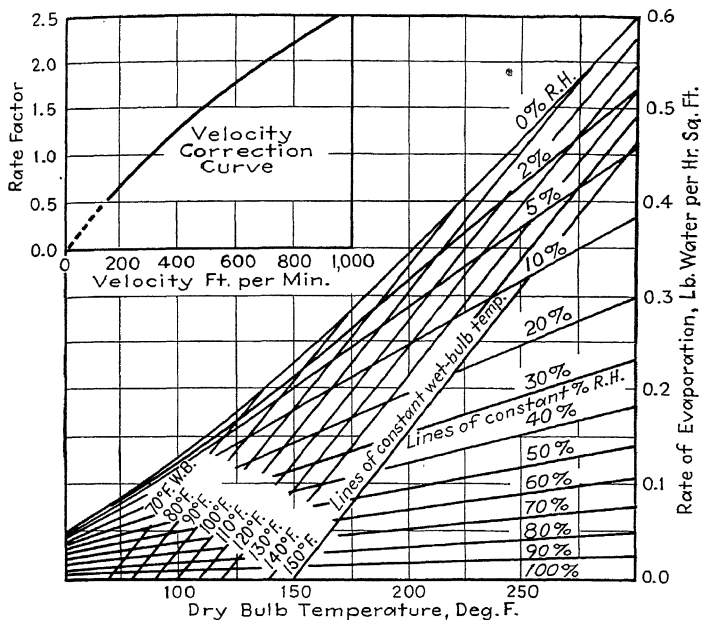


FIG. 112.—Evaporation chart for free water surface. (C. B. Shepherd, C. Hadlock, and R. C. Brewer, *Industrial and Engineering Chemistry*, 1938.)

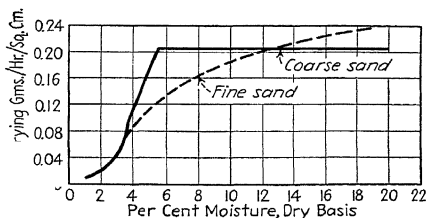


FIG. 113.—Drying rates of sand-water mixes. (After Sherwood.)

to the surface and rapidly becomes less as the drying proceeds. It is believed that beyond the critical point, the continuous surface film is broken and the water surface recedes into the

capillaries, giving the light color to the clay at this stage. As the drying proceeds, more and more of the water is converted inside the structure into vapor, making it necessary for this to travel out through the nearly empty capillaries to the surface.

In Fig. 114, an attempt has been made to show how an enlarged section of the clay would look at various stages of the drying

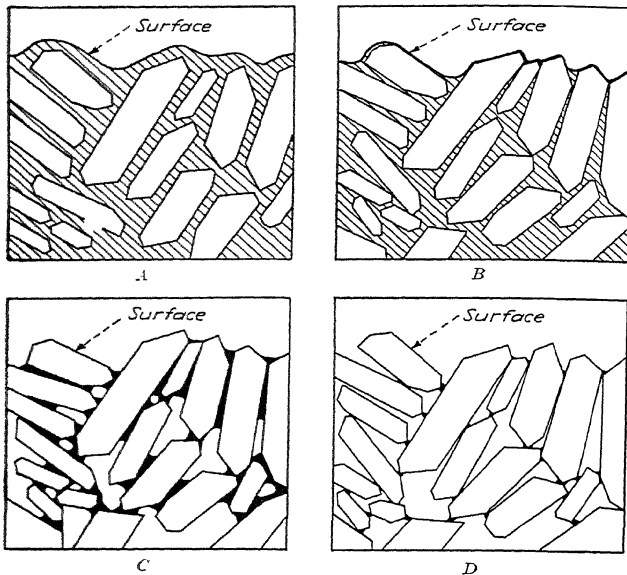


FIG. 114.—Enlarged section drawings of clay at various stages of drying.

process. In *A*, the clay particles are well separated by a water film, which also runs continuously over the surface. In *B*, the amount of water has decreased until the particles touch one another, but there is still a continuous surface film. In *C*, the water has decreased until the surface layer is broken and the level recedes into the capillaries with some air in the structure. Water is brought to the surface by a capillary flow and as vapor. In *D*, the water has still further decreased until it is found only in a few places where the particles come closest together. Here

all the transfer of water is in the form of vapor. These four conditions are shown on the typical drying-rate curve for a clay in Fig. 115.

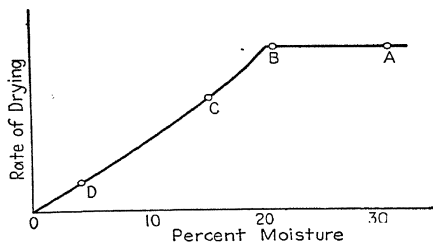


FIG. 115.—A typical drying-rate curve for a clay.

The last of the water comes off slowly because it is adsorbed on the surface of the dry particles. Practically, however, it is never necessary to remove the last trace of water. In fact, a bone-dry piece is apt to be brittle and hard to handle.

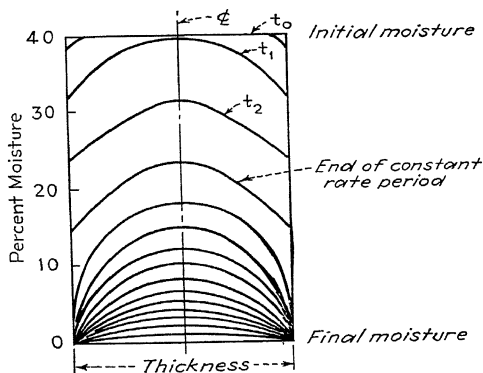


FIG. 116.—The moisture distribution across a slab of drying clay.

Moisture Gradient in Clay Body.—The moisture distribution across a slab of drying clay may be shown to follow the lines in Fig. 116. At the critical point, the moisture at the surface drops rapidly toward zero. In the constant-rate period, however, the curves are parallel and may be expressed mathematically

by Newton's law of diffusion

$$\frac{\delta M}{\delta \theta} = K \frac{\delta^2 M}{\delta x^2}$$

in the same way as for heat flow. Here

M = the moisture concentration per unit volume

θ = the time

x = the distance from the surface

K = a constant

The solution of this equation and its application to the constant-rate period has been carried out by Gilliland and Sherwood,⁽¹⁰⁾ which permits the calculation of the moisture distribution in a slab after any time interval. Reference should be made to the original papers for a full discussion of this calculation.

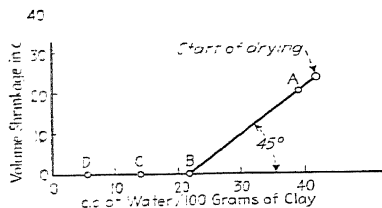


FIG. 117.—Theoretical drying-shrinkage curve of clay.

2. Drying Shrinkage.—The drying shrinkage of a clay or body is an important characteristic because it largely governs the maximum safe rate of drying. The drying-shrinkage curve is very helpful in studying some phases of the clay-water system.

Mechanism of Drying Shrinkage.—The mechanism of shrinkage is a very simple one. If the volume shrinkage is plotted against the volume of water in the clay, as in Fig. 117, it will be seen that the shrinkage curve is a straight line with a 45-deg. slope. In other words, the volume shrinkage is just equal to the volume of water lost in drying down to the critical point, where the inter-particle film becomes so thin that the particles touch one another and shrinkage can go no further. This will be made clearer by referring back to Fig. 114, which shows the condition of the clay and water at the points lettered on the curve of Fig. 117.

The water lost from the clay in drying between its original condition and the critical point is often referred to as "shrinkage water," and the remainder as "pore water."

The critical point is not usually so sharply defined as shown in Fig. 117, nor does the lower end of the shrinkage curve always lie along the axis. When clays of the swelling type, such as bentonite, are present, the curve is above the axis and only shrinks the final amount just before dryness, because of the

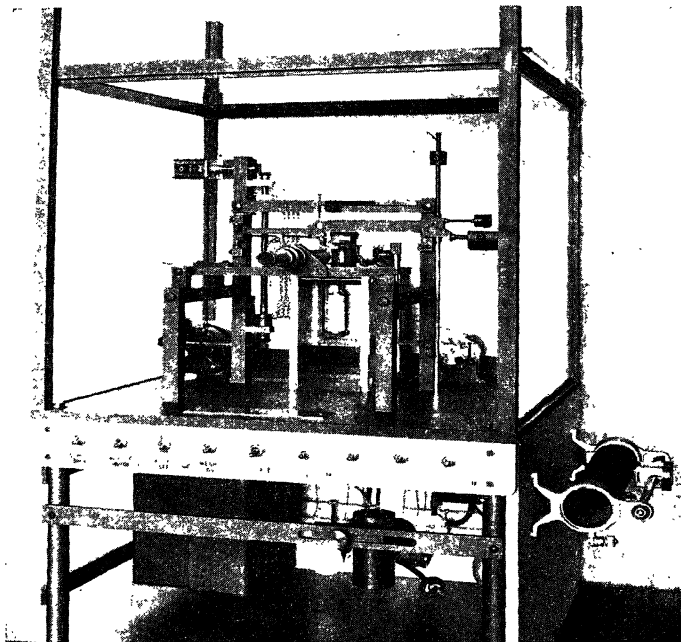


FIG. 118.—Apparatus for determining drying shrinkage.

fact that the last of the water is more firmly held between the crystal layers than on the surface of the particles. Other clays have shrinkage curves falling below the axis as a result, at the end of the drying process, of a slight expansion that has not yet been explained but is perhaps due to the opening up of kaolinite books on losing the last trace of water. ✓

Measurement of Drying Shrinkage.—Shrinkage can be measured by either a length change or a volume change. The former is

more useful for studying the type of shrinkage curve, whereas the latter gives more accurately the over-all shrinkage.

The apparatus^{22a} shown in Fig. 118 is a convenient one for obtaining shrinkage curves. The test specimen is in the form of a hollow cylinder $\frac{7}{8}$ in. outside diameter, 2 in. long, with a $\frac{1}{8}$ -in. wall. It is placed on an automatic balance in a chamber with controlled humidity and temperature; accordingly the

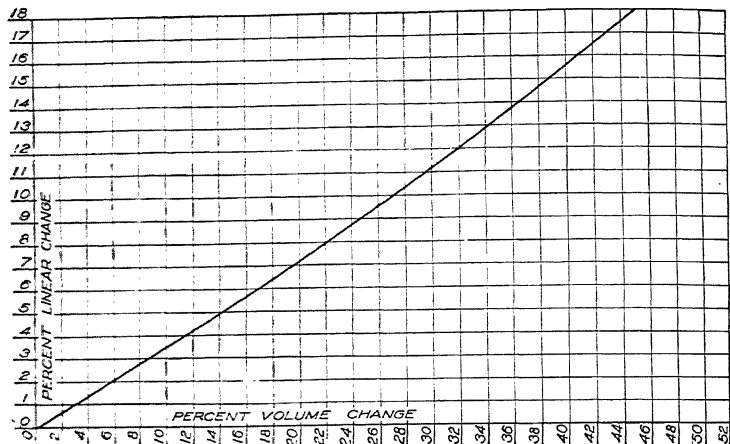


Fig. 119.—Curve for the conversion of volume to linear shrinkage based on initial dimensions.

change in length can be precisely determined with a micrometer telescope.

Volume shrinkage is usually measured by placing the specimen, at various stages of dryness, in a mercury volumeter. Volume shrinkage can be converted to linear shrinkage by the curve in Fig. 119 or by Tables 35 and 36.

Water-film Thickness.—The ceramist is much interested in the thickness of the water film separating the clay particles. If the total linear shrinkage and the number of films per unit length are known, this factor can be readily calculated. The total shrinkage can be easily determined, but the number of films is more difficult to estimate. The most careful work on this subject is by Whittaker,⁽²³⁾ who measured the drying shrinkage

TABLE 35

Four-figure table for converting:

1. Volume drying shrinkage (percentage of plastic volume) to linear drying shrinkage (percentage of plastic length).
2. Volume of firing shrinkage (percentage of unfired or dry volume) to linear firing shrinkage (percentage of unfired or dry length).
3. Volume of expansion (percentage of final volume) to linear expansion (percentage of final length).

(Courtesy of Dr. A. E. R. Westman, American Ceramic Society)

	Per- centage volume change	Percentage volume change										Differ- ences	
		0.0	Percentage linear change										
		0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9				
		0.000	0.033	0.067	0.100	0.134	0.167	0.200	0.234	0.267	0.301	0.034	
		0.334	0.368	0.402	0.435	0.469	0.503	0.536	0.570	0.604	0.638	0.034	
		0.672	0.705	0.739	0.773	0.806	0.840	0.874	0.908	0.942	0.976	0.034	
		1.010	1.044	1.078	1.112	1.146	1.181	1.215	1.249	1.283	1.317	0.034	
		1.352	1.386	1.420	1.455	1.489	1.523	1.558	1.592	1.626	1.661	0.034	
		1.695	1.730	1.764	1.799	1.834	1.868	1.903	1.937	1.972	2.007	0.035	
		2.041	2.076	2.111	2.146	2.181	2.216	2.251	2.285	2.320	2.355	0.035	
		2.390	2.425	2.460	2.495	2.530	2.565	2.600	2.635	2.671	2.706	0.035	
		2.741	2.776	2.812	2.847	2.882	2.918	2.953	2.989	3.023	3.059	0.035	
9		3.095	3.130	3.166	3.201	3.237	3.273	3.308	3.344	3.380	3.415	0.036	
10		3.451	3.487	3.523	3.559	3.594	3.630	3.666	3.702	3.738	3.774	0.036	
		3.810	3.846	3.882	3.918	3.954	3.990	4.027	4.063	4.099	4.135	0.036	
12		4.172	4.208	4.244	4.281	4.317	4.354	4.390	4.426	4.463	4.500	0.036	
13		4.536	4.572	4.609	4.646	4.683	4.719	4.756	4.793	4.830	4.867	0.037	
14		4.903	4.940	4.977	5.014	5.051	5.088	5.125	5.162	5.199	5.236	0.037	
15		5.273	5.310	5.348	5.385	5.422	5.459	5.497	5.534	5.571	5.609	0.037	
		5.646	5.684	5.721	5.759	5.797	5.834	5.872	5.910	5.947	5.984	0.037	
16		6.022	6.060	6.098	6.136	6.174	6.212	6.250	6.287	6.325	6.363	0.038	
18		6.401	6.439	6.477	6.515	6.553	6.592	6.630	6.668	6.706	6.745	0.038	
19		6.783	6.822	6.860	6.899	6.937	6.975	7.014	7.052	7.091	7.130	0.038	
20		7.168	7.207	7.246	7.284	7.323	7.362	7.401	7.440	7.479	7.518	0.039	
		7.557	7.596	7.635	7.674	7.713	7.752	7.791	7.831	7.870	7.909	0.039	
22		7.949	7.988	8.027	8.067	8.106	8.146	8.185	8.225	8.265	8.304	0.039	
23		8.344	8.383	8.423	8.463	8.503	8.543	8.582	8.622	8.662	8.702	0.040	
24		8.742	8.782	8.822	8.862	8.903	8.943	8.983	9.023	9.063	9.104	0.040	
25		9.144	9.184	9.225	9.265	9.306	9.346	9.387	9.428	9.468	9.509	0.040	
		9.550	9.590	9.631	9.672	9.713	9.754	9.795	9.836	9.877	9.918	0.040	
27		9.959	10.00	10.04	10.08	10.12	10.16	10.21	10.25	10.29	10.33	0.040	
28		10.37	10.41	10.45	10.50	10.54	10.58	10.62	10.66	10.71	10.75	0.040	
29		10.79	10.83	10.87	10.91	10.96	11.00	11.04	11.08	11.13	11.17	0.040	
30		11.21	11.25	11.29	11.34	11.38	11.42	11.46	11.51	11.55	11.59	0.040	
		11.63	11.68	11.72	11.76	11.81	11.85	11.89	11.93	11.98	12.02	0.040	
31		12.06	12.11	12.15	12.19	12.23	12.28	12.32	12.37	12.41	12.45	0.040	
32		12.50	12.54	12.58	12.63	12.67	12.72	12.76	12.80	12.85	12.89	0.040	
33		12.93	12.97	13.02	13.07	13.11	13.15	13.20	13.24	13.29	13.33	0.040	
34		13.38	13.42	13.47	13.51	13.55	13.60	13.64	13.69	13.74	13.78	0.040	
		13.82	13.87	13.91	13.96	14.00	14.05	14.09	14.14	14.18	14.23	0.040	
35		14.27	14.32	14.36	14.41	14.46	14.50	14.55	14.59	14.64	14.68	0.050	
36		14.73	14.78	14.82	14.87	14.91	14.96	15.01	15.05	15.10	15.14	0.050	
37		15.19	15.24	15.28	15.33	15.38	15.42	15.47	15.52	15.56	15.61	0.050	
38		15.66	15.70	15.75	15.80	15.84	15.89	15.94	15.99	16.03	16.08	0.050	
		16.13	16.18	16.23	16.27	16.32	16.37	16.41	16.46	16.51	16.56	0.050	
41		16.60	16.65	16.70	16.75	16.80	16.84	16.89	16.94	16.99	17.04	0.050	
42		17.09	17.14	17.18	17.23	17.28	17.33	17.38	17.43	17.48	17.53	0.050	
43		17.57	17.62	17.67	17.72	17.77	17.82	17.87	17.92	17.97	18.02	0.050	
44		18.07	18.12	18.17	18.22	18.27	18.32	18.37	18.42	18.47	18.52	0.050	
		18.57	18.62	18.67	18.72	18.77	18.82	18.87	18.92	18.97	19.02	0.050	
46		19.07	19.12	19.18	19.23	19.28	19.33	19.38	19.43	19.48	19.53	0.050	
47		19.59	19.64	19.69	19.74	19.79	19.84	19.90	19.95	20.00	20.05	0.050	
48		20.10	20.16	20.21	20.26	20.31	20.37	20.42	20.47	20.52	20.58	0.050	
49		20.63	20.68	20.74	20.79	20.84	20.90	20.95	21.00	21.06	21.11	0.050	

TABLE 36

Four-figure table for converting:

1. Volume of drying shrinkage (percentage of dry volume) to linear drying shrinkage (percentage of dry length).
2. Volume of firing shrinkage (percentage of fired volume) to linear firing shrinkage (percentage of fired length).
3. Volume of expansion (percentage of initial volume) to linear expansion (percentage of initial length).

(Courtesy of Dr. A. E. R. Westman, American Ceramic Society)

Percentage volume change	Percentage volume change										Differ- ences
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
	Percentage linear change										
0	0.000	0.032	0.067	0.100	0.133	0.166	0.200	0.233	0.266	0.299	0.033
1	0.332	0.365	0.398	0.431	0.464	0.497	0.530	0.563	0.596	0.629	0.033
2	0.662	0.695	0.728	0.761	0.794	0.826	0.859	0.892	0.925	0.957	0.033
3	0.990	1.023	1.055	1.088	1.121	1.153	1.186	1.218	1.251	1.283	0.033
4	1.316	1.348	1.381	1.413	1.446	1.478	1.510	1.543	1.575	1.607	0.033
5	1.640	1.672	1.704	1.736	1.769	1.801	1.833	1.865	1.897	1.929	0.032
6	1.961	1.993	2.025	2.057	2.089	2.121	2.153	2.185	2.217	2.249	0.032
7	2.281	2.313	2.345	2.376	2.408	2.440	2.472	2.503	2.535	2.567	0.032
8	2.599	2.630	2.662	2.693	2.725	2.757	2.788	2.820	2.851	2.883	0.032
9	2.914	2.946	2.977	3.009	3.040	3.071	3.103	3.134	3.165	3.196	0.031
10	3.228	3.259	3.291	3.322	3.353	3.384	3.415	3.446	3.478	3.509	0.031
11	3.540	3.571	3.602	3.633	3.664	3.695	3.726	3.757	3.788	3.819	0.031
12	3.850	3.881	3.912	3.943	3.973	4.004	4.035	4.066	4.097	4.127	0.031
13	4.158	4.189	4.219	4.250	4.281	4.311	4.342	4.373	4.403	4.434	0.031
14	4.464	4.495	4.525	4.556	4.586	4.617	4.647	4.678	4.708	4.739	0.030
15	4.769	4.799	4.830	4.860	4.890	4.921	4.951	4.981	5.011	5.042	0.030
16	5.072	5.102	5.132	5.162	5.192	5.222	5.253	5.283	5.313	5.343	0.030
17	5.373	5.403	5.433	5.463	5.493	5.523	5.553	5.583	5.612	5.642	0.030
18	5.672	5.702	5.732	5.762	5.791	5.821	5.851	5.881	5.910	5.940	0.030
19	5.970	6.000	6.029	6.059	6.088	6.118	6.148	6.177	6.206	6.236	0.030
20	6.266	6.295	6.325	6.354	6.384	6.413	6.443	6.472	6.501	6.531	0.029
21	6.560	6.590	6.619	6.648	6.678	6.707	6.736	6.765	6.795	6.824	0.029
22	6.853	6.882	6.911	6.940	6.970	6.999	7.028	7.057	7.086	7.115	0.029
23	7.144	7.173	7.202	7.231	7.260	7.289	7.318	7.347	7.376	7.405	0.029
24	7.434	7.463	7.491	7.520	7.549	7.578	7.607	7.635	7.664	7.693	0.029
25	7.722	7.750	7.779	7.808	7.836	7.865	7.894	7.922	7.951	7.980	0.029
26	8.008	8.037	8.065	8.094	8.122	8.151	8.179	8.208	8.236	8.265	0.028
27	8.293	8.322	8.350	8.378	8.407	8.435	8.463	8.492	8.520	8.548	0.028
28	8.577	8.605	8.633	8.661	8.690	8.718	8.746	8.774	8.802	8.831	0.028
29	8.859	8.887	8.915	8.943	8.971	8.999	9.027	9.055	9.083	9.111	0.028
30	9.139	9.167	9.195	9.223	9.251	9.279	9.307	9.335	9.363	9.391	0.028
31	9.418	9.446	9.474	9.502	9.530	9.557	9.585	9.613	9.641	9.668	0.028
32	9.696	9.724	9.751	9.779	9.807	9.834	9.862	9.890	9.917	9.945	0.027
33	9.972	10.000	10.027	10.055	10.082	10.110	10.137	10.164	10.191	10.218	0.030
34	10.245	10.272	10.300	10.327	10.354	10.381	10.408	10.435	10.462	10.489	0.030
35	10.516	10.543	10.570	10.597	10.624	10.651	10.678	10.705	10.732	10.759	0.030
36	10.786	10.813	10.840	10.867	10.894	10.921	10.948	10.975	11.002	11.029	0.030
37	11.056	11.083	11.110	11.137	11.164	11.191	11.218	11.245	11.272	11.299	0.030
38	11.326	11.353	11.380	11.407	11.434	11.461	11.488	11.515	11.542	11.569	0.030
39	11.596	11.623	11.650	11.677	11.704	11.731	11.758	11.785	11.812	11.839	0.030
40	11.867	11.894	11.921	11.948	11.975	12.002	12.029	12.056	12.083	12.110	0.030
41	12.137	12.164	12.191	12.218	12.245	12.272	12.299	12.326	12.353	12.380	0.030
42	12.407	12.434	12.461	12.488	12.515	12.542	12.569	12.596	12.623	12.650	0.030
43	12.677	12.699	12.721	12.743	12.765	12.787	12.809	12.831	12.853	12.875	0.030
44	12.922	12.945	12.968	12.990	13.013	13.035	13.058	13.080	13.103	13.125	0.030
45	13.149	13.171	13.193	13.215	13.237	13.259	13.281	13.303	13.325	13.347	0.030
46	13.44	13.47	13.50	13.52	13.55	13.57	13.60	13.62	13.65	13.68	0.030
47	13.70	13.73	13.75	13.78	13.81	13.83	13.86	13.88	13.91	13.93	0.030
48	13.96	13.99	14.01	14.04	14.06	14.09	14.11	14.14	14.17	14.19	0.030
49	14.22	14.24	14.27	14.29	14.32	14.34	14.37	14.39	14.42	14.44	0.030
50	14.47	14.50	14.52	14.55	14.57	14.60	14.62	14.65	14.67	14.70	0.030

of a number of monodisperse size fractions of a kaolin. Provided the size of the particles is known, the number of films are readily computed. The only uncertain factor is the shape of the particles, which were assumed to be plates one-third as thick as they were long and wide. In this way, he found a value of about 0.002μ as the film thickness, or a layer of about 20 water molecules. This value can also be computed by determining the thickness of the shrinkage water when spread

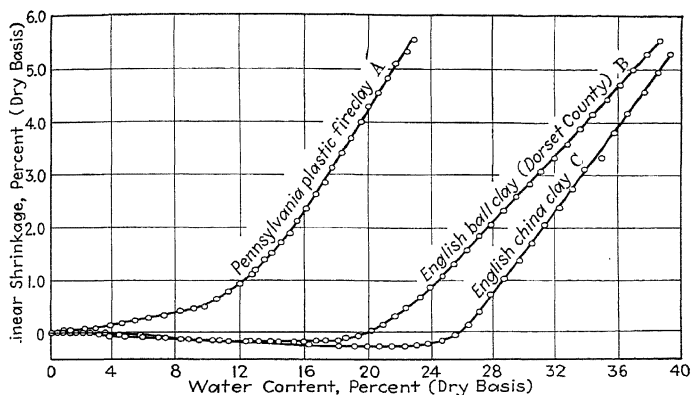


FIG. 120.—Drying-shrinkage curves of typical clays.

over an area equal to the surface area of the particles. The result is about 0.005μ , a somewhat larger figure but of the same order of magnitude.

Shrinkage Curves.—Figure 120 illustrates drying-shrinkage curves for a few typical clays. Curve A for a fireclay gives the typical secondary shrinkage, and curves B and C show a slight expansion.

3. Dry Strength.—The dry, or “green,” strength of clays is a unique and more or less unexplained property. Such theories as postulate molecular cohesion, felting of the particles, or organic colloids are not entirely substantiated as yet. It is known that the dry strength increases as the area of the particles increase (finer particles). Also the strength increases with more of some adsorbed ions. For example, a kaolin having a strength (modulus of rupture) of 400 lb. per sq. in. when dialyzed showed

an increase to 1,000 lb. per sq. in. when saturated with sodium ions. These facts indicate that strength is due, at least in part, to attractive forces between the clay mineral crystals. This is an excellent field for further research.

4. Factors Influencing Drying Efficiency.—When clayware is dried, the operation must be carried out as rapidly as possible in order to cut down the size and cost of the drying equipment. Great strides have been made in the last ten or fifteen years in

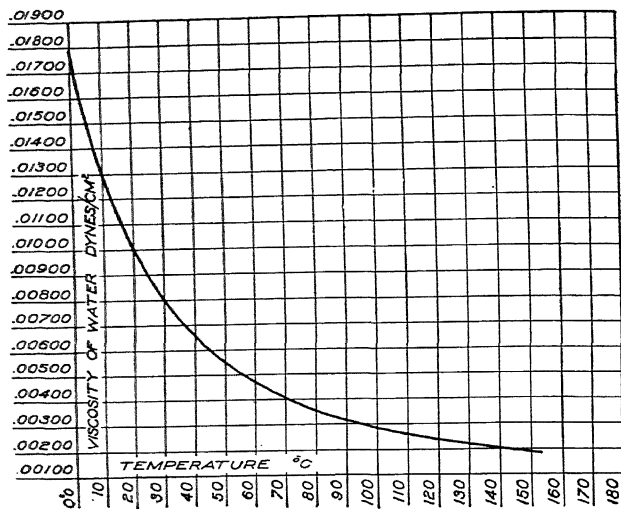


FIG. 121.—The variation of the viscosity of water with temperature.

increasing the speed and efficiency of drying by means of controlled humidity driers.

Maximum Drying Rate.—The maximum drying rate is determined by the stresses set up in the ware and the ability of the body to resist them. The same factors apply as will be discussed in Chap. XV for spalling. The tendency to crack for similar-sized pieces is a function of the moisture gradient, the slope of the shrinkage curve, and the flexibility of the structure. The only variable that can be controlled in the drying operation is the moisture gradient; and for a given rate of drying, this

can be decreased only by reducing the viscosity of the water flowing through the capillaries. The viscosity of water decreases quite rapidly with temperature, as shown in Fig. 121, which explains the reason why, in modern driers, the ware is heated rapidly to the maximum temperature in a saturated atmosphere before much drying takes place.

The size of the refractory piece influences the time required to dry. Macey⁽¹³⁾ has shown that under constant drying conditions, various sizes of cubes dry in times proportional to the length of the edge of the cube. Also the larger the piece the greater will be the tendency to crack under given drying conditions. It should also be realized that when the water content is sufficiently low to come below the critical point, the shrinkage stops and therefore the drying can be carried on as rapidly as desired, provided the vapor can escape from the interior without setting up a bursting pressure.

Examples of Drying.—As a concrete example, the problem of drying a brick as rapidly as possible when made from a mechanically weak, high-shrinking clay will be considered. In order to prevent too rapid surface evaporation, no artificial velocity was imparted to the air and the humidity was kept at a maximum. It was then necessary only to find the maximum temperature that could be used without cracking the brick. It should be realized that if the brick could be heated uniformly and at a rapid rate, the drying could proceed with extreme rapidity because of the high diffusion rate at elevated temperatures. However, it takes some time for the center of the brick to reach the temperature of the surface; and the resultant temperature gradient will, of course, increase the moisture gradient, which, as explained before, is the limiting factor in the rate of drying.

The apparatus used for the experiments consisted of a closed chamber with the brick suspended on a platform in the center of it. The heat was supplied by an electric heating coil so that any desired temperature could be easily obtained. The chamber, in each case, was brought up to the desired temperature, and the wet, cold brick was put in. Arrangements were made to obtain the weight of the brick continuously throughout the drying process. Figure 122 shows the curves for the rate of drying for various temperature conditions. A brick dried under condition *D* showed no signs of cracking. Under condition *C*,

a few slight cracks appeared on the surface; whereas under conditions *A* and *B*, the bricks were quite badly cracked.

Distribution of Heat.—It is quite a step from drying a single brick in the laboratory to drying a full car in a production drier. Circulation of air must be adjusted both to bring heat to the brick at the required rate and, at the same time, to carry away the water vapor. In order to dry all the bricks alike, a large volume of air must be circulated with the proper distribution of velocity.

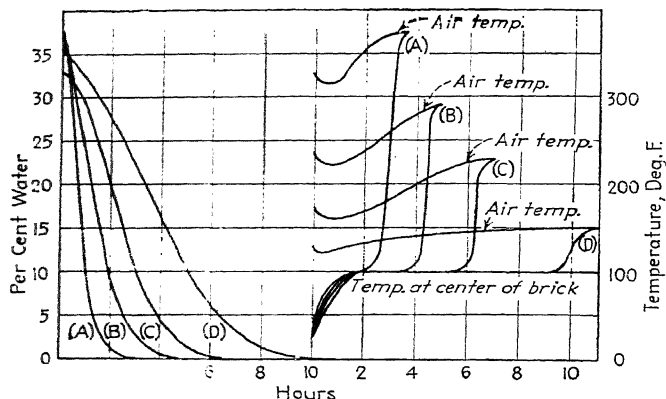


FIG. 122.—Curves showing the rate of drying of bricks under various temperature conditions.

Conservation of Heat.—A definite amount of heat is required to evaporate the water; but in addition, heat must be supplied for the waste air leaving the drier, for the heat in the bricks, and for the loss through the drier walls. Therefore, an efficient drier will have a minimum volume of exit gases, by means of recirculation, and will have well-insulated walls.

5. Drier Calculations.—It is not within the scope of this book to consider drier design, as this is well covered in more general treatises. However, it might be well to point out some of the principles involved. The heat content of the air supplied to the drier, between the entrance and exit temperatures, must be sufficient to provide for the heat required in the drying operation. Also the volume of the air passing through the drier must be so

DRYING

great that the moisture added to it will not bring it above the saturation point at the exit temperature (or temperature of the entering bricks).

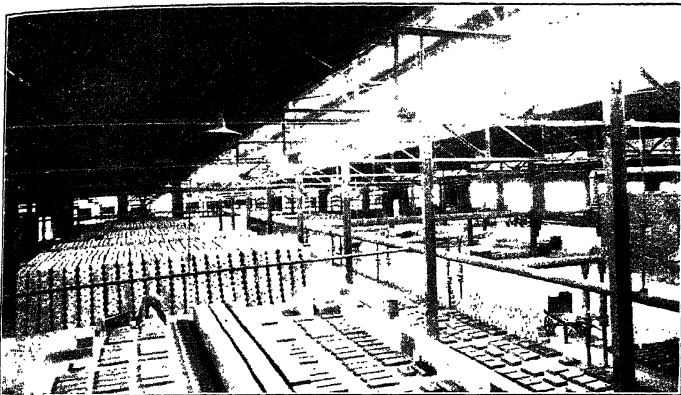


FIG. 123.—A modern hot floor. (Courtesy of United States Refractories Corporation.)

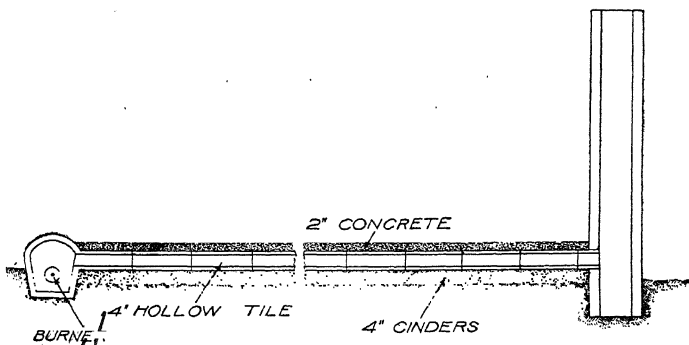


FIG. 124.—Section showing construction of a direct-fired hot floor.

6. Types of Driers.—The hot floor is used to a considerable extent at the present time for drying and tempering soft-mud bricks and for drying large shapes. The modern hot floor is usually constructed as shown in Fig. 123. The heat is supplied by means of steam pipes running in conduits or tiles just under the

surface of a concrete floor. The temperature of the floor can be controlled by valves, and the floor is usually divided up into small sections so that the temperature can be regulated according to the material drying at any particular point on the floor. Hot floors are sometimes heated by waste heat from the kilns or by direct heat from coal or oil fires, from which the hot gases pass under the floor in tile flues, as shown in Fig. 124. These methods, however, are not so satisfactory as steam heating

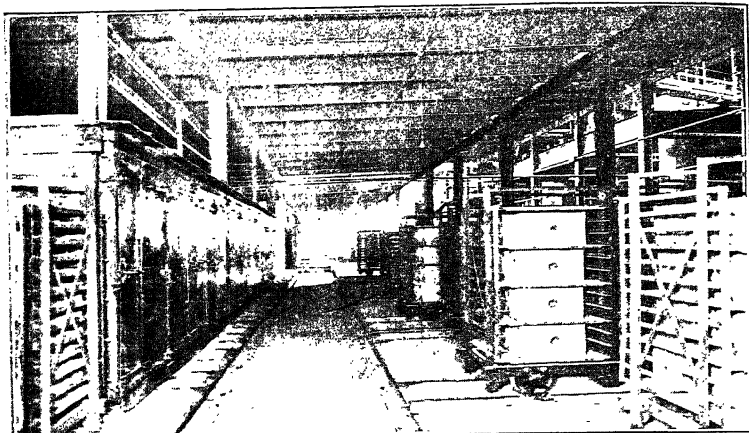


FIG. 125.—The entrance end of a group of tunnel driers. (Courtesy of Harbison-Walker Refractories Company.)

because it is difficult to control the temperature of the floor and because the temperature will vary considerably from one end of the floor to the other. Sometimes, the thickness of the floor is varied from the hot to the cold end to give a more even surface temperature. From one-half to four 9-in. equivalents can be dried per square foot of floor per 24 hr., depending on the clay, the water content, and the size. In some plants, one-half of the drier capacity is in the hot floor. -

Tunnel driers are used mainly for bricks and small shapes. They consist of a long tunnel in which rack cars of bricks can be placed. Heat is supplied by steam coils under the tracks or, in some cases, by waste heat which passes through the tunnel. The green bricks are usually pushed into the tunnel at the cooler

end and gradually progress to the hotter end until they are completely dry. Figure 125 shows a tunnel of this type. The bricks or shapes are placed on shods that are held in the rack cars as shown in Fig. 126. Sometimes perforated shods are used to speed up the drying of the underside of the bricks. They cannot be used, however, with very soft clay, for they will mark the brick.

The more modern type of drier is the continuous-tunnel type, in which the loaded cars are pushed at a uniform rate through

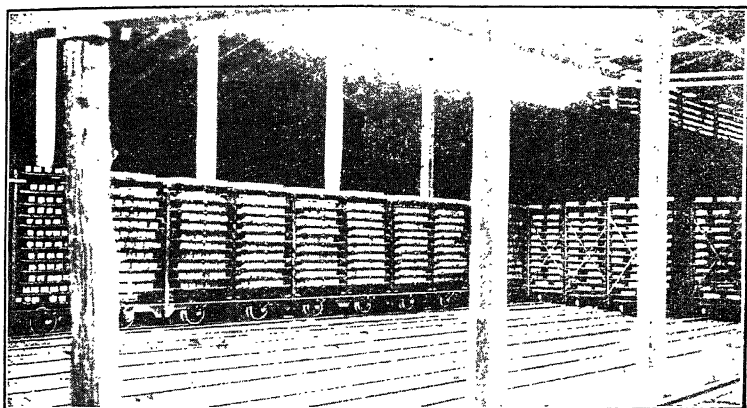


FIG. 126.—Bricks on rack cars ready to enter a drier. (Courtesy of Koppel Industrial Car Equipment Company.)

a tunnel having carefully regulated temperature and humidity values at each section. Fans or injectors are used to circulate the air around the steam coils and through the bricks in order to ensure a rapid and uniform transfer of heat to the drying material. Usually recirculation is used; *i.e.*, the air is passed around a closed circuit, the only vent being a small escape pipe at the top of the tunnel to allow the moisture from the bricks to pass off. The tunnel is divided longitudinally into sections, and each section is controlled for temperature and humidity by automatic controllers. In general, the temperature and humidity are high at the start to heat the brick with little loss of water from the surface. The humidity is then gradually decreased as the bricks pass through the tunnel. The regulation,

however, must be determined for the particular kind of clay being dried. Figure 127 illustrates a drier of this type. In Fig. 128 is shown a temperature schedule⁽⁴⁰⁾ for this drier.

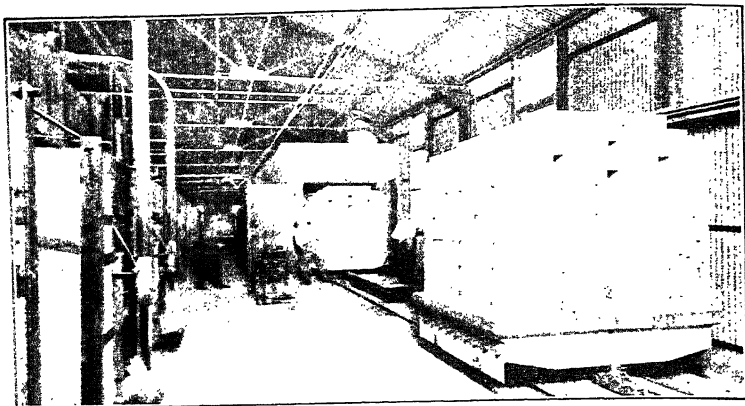


FIG. 127.—A continuous tunnel drier. It will be seen that the bricks are piled on the tunnel kiln cars and will not have to be transferred again. (Courtesy of A. P. Green Fire Brick Company.)

The temperature in driers varies according to the nature of the clay and size of the articles. Generally it is kept as high as possible, 50°C. (122°F.) to 90°C. (194°F.). The capacity of a

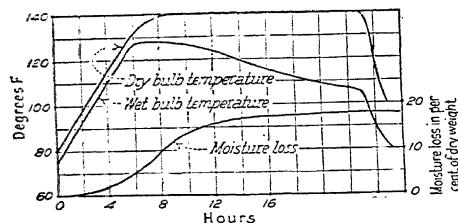


FIG. 128.—A typical drying schedule for firebrick in a modern humidity drier. (J. Am. Ceram. Soc.)

drier depends also upon the clay and the size of the articles. It is an economy to dry as rapidly as possible, as this reduces the investment in the drier, cars, and shods for a given output. Typical drying conditions are shown in Table 37.

Since the design and construction of efficient driers require considerable technical knowledge and experience, the amateur drier builder seldom turns out a satisfactory job. The scientific

TABLE 37.—DRIER CONDITIONS

Type of brick	Maximum drier temperature		Time to dry 9-in. brick, hr.
	°F.	°C.	
Hand-molded.....	160	71	48
Stiff mud, re-pressed...	160	71	24
Silica.....	150-250	66-121	24
Chrome and magnesite	180	82	16
Insulating firebrick....	180	82	30

study of drying problems has lately resulted in great advances in this field. The following references should be consulted for the details of drier design.

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CHAPTER IX

THE FIRING OF CLAY AND OTHER REFRACTORY MATERIALS

1. Effect of Heat on Raw Clay.—One of the most important steps in the manufacture of refractories is the firing process, whereby the raw clay is profoundly altered into a strong and partly vitreous mass. The steps occurring in the process are particularly important, as they guide us in the proper heat-treatment of a clay to give the greatest efficiency in firing and the most satisfactory finished product.

Methods of Measuring Heating Changes.—The changes that occur in a clay on heating, though not at once evident, can be indirectly observed through a number of secondary alterations which may be detected by the proper type of measurement. One of the most obvious changes taking place in a heated clay is the loss in weight. This weight loss can be measured by placing a sample of clay in a constant-temperature furnace ^(21a) and holding it at one temperature until the weight becomes constant, then increasing the temperature another step and holding it again, and so on until the clay loses no further weight. Also, the weight loss can be determined by raising the temperature of the sample at a predetermined rate and recording the weight of the specimen as a continuous function of time. The weight loss is due (1) to loss of adsorbed water at comparatively low temperatures, (2) to the loss of chemically combined water which occurs at a rather definite temperature for any particular clay mineral, and (3) loss of CO_2 and SO_2 from oxidation of carbon or the breaking up of carbonates and sulfides. The proper interpretation of the weight-loss curve of a clay will give a valuable insight into the clay constituents, as shown by the curves in Fig. 129 for a number of clay minerals. A well-crystallized mineral like kaolinite loses its chemical water substantially at one temperature, whereas an amorphous material like allophane loses it gradually.

Another characteristic of clay when heated is the absorption and evolution of heat⁽²⁸⁾ at certain temperatures, which can readily be determined by the differential thermal apparatus described in Chap. V. A typical curve of this type for a fireclay containing only the mineral kaolinite is shown in Fig. 130.

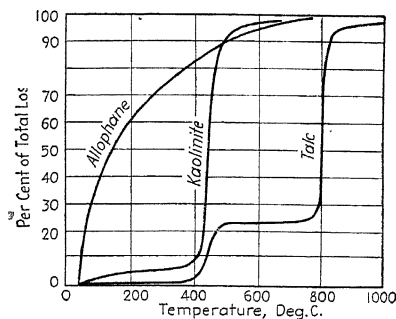


FIG. 129.—Weight-loss curves.

The slight heat absorption at 150°C. (300°F.) is due to the driving off of adsorbed water from the surface of the grains. The small heat evolution at approximately 400°C. (750°F.) is caused by the oxidation of a slight amount of organic matter in the clay. The larger absorption peak at 620°C. (1150°F.) is caused by the

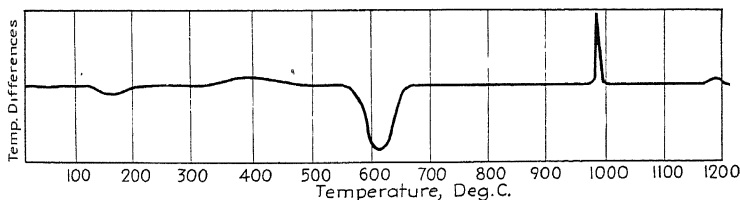


FIG. 130.—Thermal curve for a fireclay.

evolution of the chemically combined water in the kaolinite structure, and the sharp and high peak at 980°C. (1800°F.) is believed to be due to the change of amorphous alumina to the crystalline γ -form. The small peak at 1200°C. (2190°F.) is considered to be the result of the crystallization of cristobalite from the silica glass that has previously formed in the clay.

The shrinkage, and conversely the porosity, is a very characteristic property and shows quite clearly the changes that occur in the clay. A typical shrinkage curve for kaolin is shown in Fig. 131. No shrinkage occurs under this slow heating until 450°C. (840°F.) is reached, at which temperature the chemically combined water is driven off, producing a decrease in volume that continues slowly to above 900°C. (1650°F.) where a sharp decrease in volume corresponds to the formation of γ -alumina. At the same time, mullite begins to crystallize.

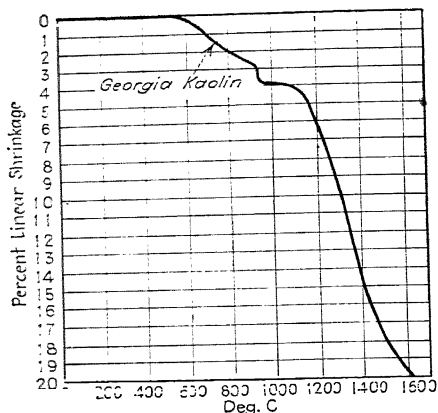


FIG. 131.—The shrinkage characteristics of a Georgia kaolin.

At 1150°C. (2100°F.), glass begins to be formed in larger quantities, which tends to pull the clay grains together, and the shrinkage continues rapidly up to the fusion point of the clay, provided bloating does not occur.

One of the most powerful tools used in studying the changes occurring in a clay is the X ray,⁽²⁵⁾ which gives us an insight into the atomic arrangements of the clay crystals and the altered products as discussed in Chap. IV. Briefly, however, the recent results of X-ray analysis indicate that kaolinite is unchanged until the chemically combined water is driven off at 450°C. (840°F.). Above this temperature, there is a noncrystalline structure called "metakaolin" about which we know very little. At 980°C. (1800°F.), the γ -alumina crystallizes; and immediately

afterward, mullite crystals can be detected^(15,19,24a) even though they are very much finer than would be visible in the microscope.

The microscope does not tell us a great deal concerning the changes occurring in the clay because they take place on such a small scale that an observation of the larger grains shows little. Until the temperature is high enough for large-sized needles of mullite to crystallize out, the microscope is of little help. However, the recently developed electron microscope allows us to observe the clay particles at a magnification of as high as 25,000 \times , whereby clay particles as small as 0.1μ can be readily seen. Recently, a very interesting study with the electron microscope by Eitel, Müller, and Radczewski⁽²⁷⁾ has been made of the breakup of kaolinite on heating to various temperatures. This is the first time that we have had direct visual proof of the reactions going on in the clay. The photographs in this paper are remarkably clear even at the very high magnification and indicate the following reactions: The original clay shows definite hexagonal plates of varying size with clear-cut edges, as reproduced in Fig. 40 of Chap. V. On heating to 500°C . (930°F .), which is sufficient to drive off the chemically combined water, the only change noted is a slight softening of the edges of the plates. At 800°C . (1470°F .), the plates show slight rounding of the corners and apparently some fine-grained material is thrown off from the edges. Whether this occurred directly in the heating or by mechanical abrasion of the now soft and friable plate is not certain. At 1000°C . (1830°F .), pseudomorphs of the original kaolinite crystals are still seen, but there is a lack of distinctness with no new crystals in evidence. At 1200°C . (2190°F .), the ground mass of the original kaolinite crystals is filled with small mullite crystals imbedded in glass.

Another characteristic change in clay on heating is the increase in hardness and mechanical strength after cooling. The raw clay, in many cases, has considerable mechanical strength; but as it is heated to drive off the adsorbed water, this strength usually decreases slightly because of the lessened attraction between the particles. When the chemically combined water is driven from the clay, there is often a further decrease in strength, due to the crystalline breakup; but at 1000°C . (1830°F .) in a pure clay, the strength begins to increase owing to the formation of glass and recrystallization of the remaining components.

The strength increases rapidly up to the softening point. In less pure clays, the increase in strength occurs at lower temperatures owing to the earlier glass formation.

Other changes to be noted are variations in color, solubility in acid, and fluorescence of certain dyes in contact with the clay. The latter is illustrated by the dye morin, which fluoresces under ultraviolet light when in contact with the alumina molecule. When clay samples fired to different temperatures are examined in this way, fluorescence will be absent up to 450°C. (840°F.) but will show strongly up to 980°C. (1800°F.) and then less strongly. This indicates the presence of the alumina molecule in the metakaolin.

Picture of the Heat Changes in a Pure Kaolin.—In summing up the evidence obtained from the preceding observations of the various changes in the physical properties of a clay, one may start in with a drying temperature of 100°C. (212°F.). At this temperature, a considerable amount of adsorbed water still adheres to particles, and the finer the clay the larger amount of this water. It is not driven off at any one temperature, but over a considerable range; the more firmly attached water molecules are held until the higher temperatures. This adsorbed water can be removed at low temperatures by confining in an atmosphere free from water vapor, but a considerable amount of time is required. At a temperature of 450°C. (840°F.), the chemically combined water or, more correctly speaking, the OH groups are removed from the kaolinite molecule. It has been shown that with very careful temperature control and long time of heating, this water is driven off very completely at a single temperature, as indicated by the weight-loss curve in Fig. 129 which was taken under carefully controlled conditions. However, even under this condition, there is a small amount of remaining water that is not driven off until 700 or 800°C. (1290 or 1470°F.) is reached. It is a little difficult to understand just what part of the lattice is occupied by these OH groups which are so firmly held. More probably the gradual weight loss is due to adsorbed water molecules both below and above the crystalline breakup temperature.⁴ The condition of the crystal structure between the temperature of removal of the OH groups and the crystallization of alumina has received a great deal of consideration by various authorities; but at the

present time, we seem to have no really definite pictures except that there is a noncrystalline arrangement of the atoms. On the other hand, the structure cannot be entirely broken up, as it is possible to replace the water by comparatively simple hydrothermal action, provided the clay has not been heated above 980°C. (1800°F.). Also the evidence of fluorescence indicates that a sort of alumina molecule is still in existence up to this temperature.

At approximately 980°C. (1800°F.), in the case of kaolin, there is a sudden heat evolution, which is believed to indicate the crystallization of the alumina into the γ -form. It is interesting to note that the heat effect is greatest for a silica-alumina ratio of 2:1 as it occurs in kaolinite. It is shown by Insley^(24a) that if the alumina is higher or lower than this particular ratio, the heat effect occurs over a wider range of temperature and is not nearly so marked. He believes that the silica acts in such a way as to stabilize the amorphous structure and prevent crystallization until a certain temperature is reached. This again would indicate that the structure, after the water is driven off, is not entirely random but must have some arrangement by which the alumina crystallization is influenced by the silica.

Immediately after the formation of the γ -alumina, it apparently starts dissolving in the glass and mullite begins to crystallize out. At first these crystals are so small that they can be detected only by the X rays; but at a somewhat higher temperature, they become large enough to see easily under the microscope (Fig. 132).

The heat evolution at 1200°C. (2190°F.) is believed to be due to crystallization of cristobalite from the glass.^(24a) Such crystals have been detected by Insley, and this seems to be a reasonable explanation. No work has been done to determine this crystallization with less pure clays. Possibly the fluxing effect of such materials as iron oxide and lime might greatly influence it.

Effect of Heat on Clay Impurities.—Most of the fireclays contain impurities in the form of sulfides and carbonates and also carbon in the form of lignite or bitumen. As the clay is heated in an oxidizing atmosphere, a great many reactions can take place with the eventual loss of the carbon and sulfur by oxidation. There is no opportunity here to discuss these reactions completely, as they are of much more importance to the manufacturers of heavy clay products than to the manufacturers

of refractories. However, Table 38 will give the more important reactions and the temperatures at which they occur. The upper limit of the temperature is not a very definite one, as it depends on the amount of excess air in the combustion gases, the permeability of the clay, and the size of the object being



FIG. 132.—Thin section of fused kaolin. This microphotograph shows large mullite crystals embedded in silica glass. The nearly square cross section of these crystals can be seen; 750 diameters with crossed Nicol prisms and gypsum plate.

fired, as well as the interaction between the various impurities. For example, if the pores of the clay contain CO_2 from oxidation of carbon, the increased partial pressure of this gas will delay the dissociation of a material like calcium carbonate. In all firing of clays containing considerable amounts of carbon or sulfur, the initial part of the firing process must be carried out sufficiently slowly to oxidize these products completely

before the surface pores of the clay are closed; otherwise the well-known black coring will occur.

TABLE 38.—BREAKDOWN TEMPERATURES OF CLAY IMPURITIES

	°C.	°F.
$\text{FeS}_2 + \text{O}_2 \rightarrow \text{FeS} + \text{SO}_2$	350-450	660-840
$4\text{FeS} + 7\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$	500-800	930-1470
$\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3$	560-775	1040-1430
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	350 →	660 →
$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$	250-920	480-1690
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	600-1050	1110-1920
$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	400-900	750-1650
$\text{FeCO}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{CO}_2$	800 →	1470 →
$\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$	1250-1300	2280-2370

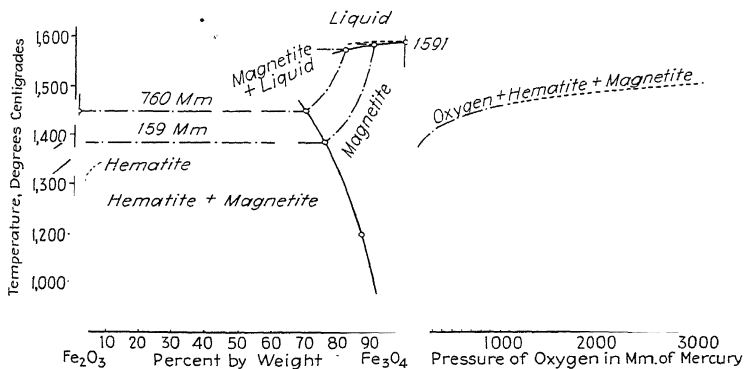


FIG. 133.—Equilibrium diagram. The diagram on the left indicates the points that have been determined on the field boundaries by circles or by arrows. The points fixing the isobars are not shown here.

The right-hand diagram gives a curve representing the relationship between the temperature and the pressure of oxygen with which magnetite + hematite can coexist in stable equilibrium. At the lower pressures it represents quite closely the true conditions. In the upper pressure region, however, it can be considered only as giving the order of magnitude of the pressure. (*Greig, Posnjak, Merwin, Sosman, Am. J. Sci.*)

The system of Fe_2O_3 - Fe_3O_4 - O_2 is shown in Fig. 133. As the temperature is increased, a higher concentration of oxygen is required to hold the same ratio of Fe to O.

Effect of Heat on Other Hydrated Minerals.—The investigation of the relations between the structures, properties, and crystallographic orientations of minerals with the OH ions and their corresponding oxides is very interesting, but to date only meager information is available.

The crystalline breakup by heat of montmorillonite and illite has recently been studied by Grim and Bradley.^(30a) Montmorillonite shows a lattice breakdown starting at 600°C. (1110°F.) and complete at 800°C. (1470°F.). A spinel phase appears at 850°C. (1560°F.) but is all dissolved at 1300°C. (2370°F.). Mullite appears at 1050°C. (1920°F.) and increases with increasing temperatures. Illite goes through the same kind of breakup, but mullite does not appear until 1100°C. (2010°F.).

Gibbsite, $\text{Al}(\text{OH})_3$, a common constituent of high-alumina clays, has a layer lattice structure in which the Al atoms lie between six OH ions and the layers are packed in such a way that each OH of one layer is opposite an OH of the next layer. At temperatures as low as 150°C. (300°F.), gibbsite loses some of the OH groups and boehmite $\text{AlO}(\text{OH})$ is formed, which on further heating above 275°C. (527°F.) forms $\gamma\text{-Al}_2\text{O}_3$,⁽²¹⁾ a kind of alumina with a spinel-like structure. A parallelism has been found between the crystallographic orientations of the original and the final crystals.

On the other hand, diaspore, which is also a common constituent of the high-alumina clays, is more stable than gibbsite and does not lose OH groups until a temperature of 350°C. (660°F.) is reached. The reason for this is evident from its crystal structure; X-ray studies show that its formula should be written HAlO_2 , and we must think of the H as a small cation in the structure in twofold coordination between a pair of oxygens. Both boehmite and diaspore are dimorphous. On dehydration of diaspore, γ -alumina is formed and, at 550°C. (1020°F.), starts to transform to corundum. The latter transformation is completed at 950°C. (1740°F.), and again there is a parallelism between the orientation of the original and the final crystals. This parallelism in crystallographic orientation illustrates the important role played by the crystal structure in the treatment of raw materials.

It is interesting to note that in a similar fashion, goethite, HFeO_2 , dehydrates to hematite, Fe_2O_3 , and brucite, $\text{Mg}(\text{OH})_2$,

forms periclase, MgO ; in both cases, the original and final crystals are in parallel aggregates. Lepidocrocite, $FeO(OH)$, transforms to $\gamma-Fe_2O_3$, which is magnetic and has a spinel-like structure.

At high temperatures, the oxides remaining from the low-temperature reactions, such as iron oxide, lime, and alkalis, react with the clay and form a glass that has a marked influence on the mechanical properties of the finished piece. The oxides also act to a certain extent as catalyzers or mineralizers to increase the rate of growth of the mullite crystals and thereby influence the finished products. It is highly desirable to produce in the clay body a sufficient amount of glass to allow recrystallization to take place and act as a bonding agent to give good mechanical strength. The lower the temperature at which this can take place the less expensive will be the burning operation. On the other hand, it is undesirable to have too much or too fluid a glass in the finished refractory; in which case, it will show deformation at temperatures so low that its use will be limited. For example, refractories made from pure kaolin must be fired at comparatively high temperatures in order to complete the firing shrinkage and produce sufficient mechanical strength; but when so fired, they give excellent refractory properties. Less pure fireclays can be initially fired at much lower temperatures owing to the more abundant formation of glass, but this glass limits their upper temperature of use.

Firing Shrinkage and Porosity of Clays.—When studying a new clay, one of the most instructive tests is the determination of the shrinkage and porosity when fired at different temperatures. This information enables the prediction of the usefulness of the clay when used in a refractory for any particular purpose.

The methods used for measuring shrinkage are comparatively simple. A series of specimens carefully formed may be fired at a number of temperatures, and a decrease in volume or a linear dimension determined for each one. Also a continuous shrinkage curve for a clay can be made by increasing the temperature at a steady rate and measuring the length of the specimen as described for shrinkage measurements in Chap. XVI. It should be noted that these values include the reversible expression. As will be explained later, to obtain consistent shrinkage measurements, the original specimens must be formed under exactly the same conditions of water content and pressure.

The porosity of the fired specimen is due to both closed pores and open pores. The usual method of determining porosity, which we call "apparent porosity" because it does not include the closed pores, may be determined by filling the pores with water or air, as described below.

The apparent porosity of a small sample is usually measured by making three weighings: the first, the dry specimen; the second, the saturated specimen immersed in water; and the third, the saturated specimen suspended in air.^(45a) It is quite necessary to be sure that the specimen is thoroughly saturated; and in order to do this, it should be boiled in water for 2 hr. Even with this precaution, there will be some closed pores that the water cannot reach; consequently this method generally gives a low value for the porosity. The porosity is determined from these three weighings by the following formula:

$$P = \frac{W - D}{W - A} \times 100$$

where P = the percentage porosity

W = the weight of saturated specimen in air

D = the weight of dry specimen in air

A = the weight of saturated specimen in water

The volume can be directly measured by a mercury volumeter to give a higher precision. The instrument described by Goodner⁽⁴¹⁾ is convenient for this purpose.

When the porosity of the full-sized brick is to be obtained, it will be found that the previous method cannot always be used because the water will run out of the pores when the weighing W is made. The porosity is best obtained in this case by a vacuum method, the principle of which is shown in Fig. 134. A brick is placed in chamber A and sealed tight. The chamber B is empty but of known volume. Chamber A is then connected to a vacuum pump and pumped down to a vacuum of about 700 mm. The connection to the pump is then closed; the connecting cock between the two chambers is opened; and the change in reading of the manometer is noted. The porosity of the brick is then calculated by the following formula, using the constants of the apparatus:

$$S = V_b \frac{P_2}{P_1 - P_2} - (V_a - V)$$

where S = the pore volume

V = the volume of specimen (bulk)

V_a = the volume of chamber A

V_b = the volume of chamber B

P_2 = the equilibrium manometer reading

P_1 = the evacuated manometer reading

The precision of the instrument can be checked at any time by measuring the porosity of a block of iron or any other non-porous material, which should, of course, work out to be zero.

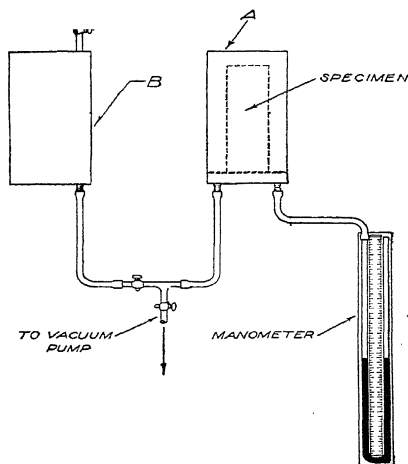


FIG. 134.—Apparatus for obtaining the porosity of a brick by the vacuum method.

This method is rapid and reasonably precise, as air can find its way into smaller pores than can water.

It will be noted in the formula given above that the bulk volume of the brick is required. In some cases where the brick is even and smooth in size, the volume can be determined by linear measurements; but usually it is better to obtain the volume directly, which is most readily accomplished by saturating the brick with melted paraffin. The surplus is carefully wiped off; the brick is then immersed in an overflow can, as shown in Fig. 135; and the displaced water weighed or measured.

The volume can also be obtained by immersion in mercury⁽⁴⁰⁾ or sand. The former method is accurate but requires consider-

able clean mercury, which is not always convenient. The latter method is simple but not very precise unless great skill is used in packing the sand to exactly the same extent each time.

The determination of the closed pores is best carried out by grinding the specimen fine enough to break into all the pore spaces and then measuring the true density of the powder by the well-known pycnometer method (Chap. XIX). From the

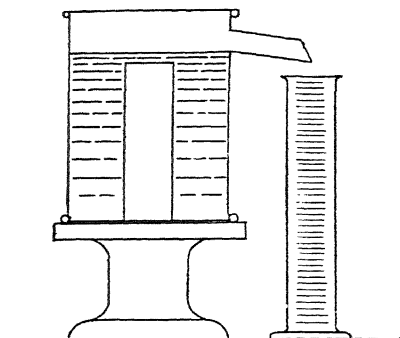


Fig. 135.—An overflow can for measuring the volume of a brick.

values of true density d_t and bulk density d_b of the original specimen, the true porosity, *i.e.*, the total volume of the closed and open pores in relation to the bulk volume, can be determined by the following formula:

$$\rho = \frac{d_t - d_b}{d_t}$$

Table 39 shows the relative amount of closed and open pores in some refractories.¹³³

TABLE 39.—PRECISION OF POROSITY DETERMINATIONS

Material	Average specific gravity	Average true porosity	Error due to closed pores by water method	Error due to closed pores by vacuum-method
Silica brick.....	2.31 to 2.33	27.2 to 28.3	0.3 to 1.9	-0.15 to -0.18
Magnesite brick.....	3.54 to 3.56	25.6 to 29.5	0.3 to 1.1	0.0 to 0.3
Flint-clay firebrick.....	2.67 to 2.72	27.7 to 32.6	3.7 to 10.2	1.5 to 7.0
Plastic-clay firebrick.....	2.66 to 2.69	22.8 to 15.9	1.0 to 4.0	0.0 to 0.3

The firing shrinkage and porosity are influenced quite markedly by the conditions under which the specimen is molded. Obviously, the more densely the raw clay is packed the less will be

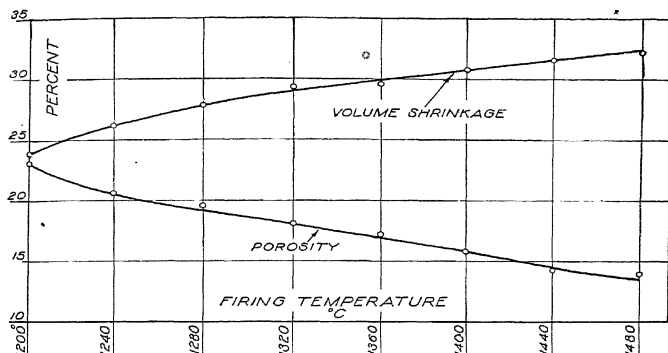


Fig. 136.—Raw smooth flint clay, Missouri. (*J. Am. Ceram. Soc.*)

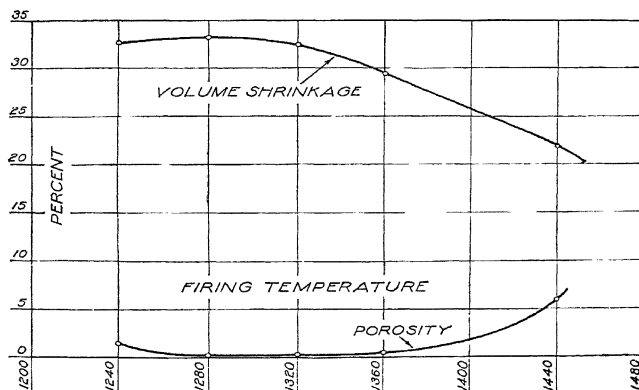


Fig. 137.—Raw plastic clay, Missouri. (*J. Am. Ceram. Soc.*)

the firing shrinkage when carried to a given final porosity. Therefore, high pressure in molding, proper water content, and the fineness of the clay all influence the amount of shrinkage.

Figures 136 to 140 show curves of shrinkage and porosity values for a number of typical fireclays. These illustrations

give a general picture of the shrinkage and porosity values of the clays; but for any particular problem, firing tests should be

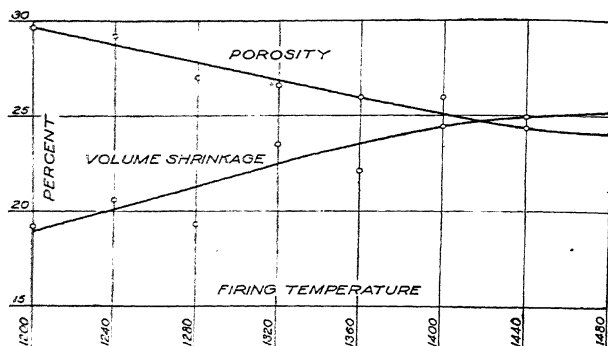


FIG. 138.—Raw burley flint clay, Missouri. (*J. Am. Ceram. Soc.*)

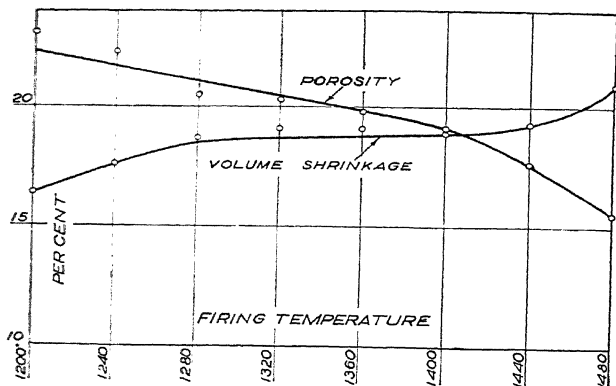


FIG. 139.—Plastic bond clay, Cambria County, Pa. (*J. Am. Ceram. Soc.*)

made under the exact conditions to which the clay will be subjected.

In Table 40 are given average porosity values for some typical refractories.

2. Firing Properties of Nonclay Refractory Materials. *Silica.* Silica, one of the most important of refractory minerals, has

received a great deal of study, and consequently more data on its properties are available than on any other mineral. The most complete treatise on silica is that of Sosman,^(66a) which

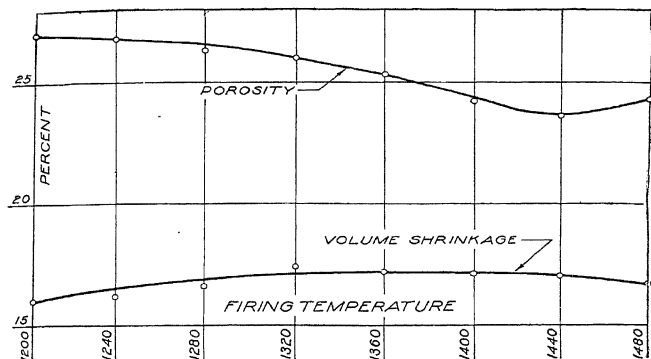


FIG. 140.—Dean flint clay, Pennsylvania. (*J. Am. Ceram. Soc.*)

TABLE 40.—POROSITY OF REFRACTORIES

Type of Brick	Average Porosity, Per Cent
Hand-molded fireclay	24
Stiff-mud fireclay	21
Dry-pressed fireclay	22
Kaolin	18
High alumina, 70 per cent	32
Magnesite	23
Magnesite, chemical bond	11
Silica	25
Forsterite	25
Chrome	23
Chrome, chemical bond	11
Tank blocks, flux	20
Tank blocks, grog	7
Tank blocks, fused	0
Silicon carbide, clay bond	20
Insulating firebrick, 2.5 lb	75
Insulating firebrick, 1 lb	90

the reader should consult for many of the details for which space is not available here.

In nature, silica is very common and most often occurs as the mineral quartz. It is found in many different types of mineral

deposits, is an essential constituent of such acid igneous rocks as granite and rhyolite, and also occurs in veins, in sedimentary rocks such as sandstones and quartzites, and in unconsolidated river and beach sands.

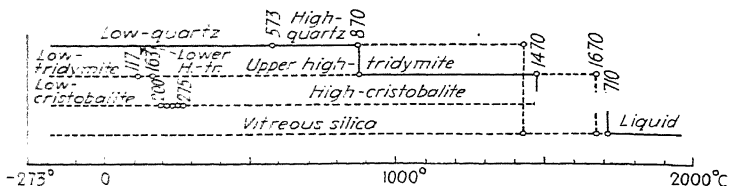


FIG. 141.—Polymorphous modifications of silica and their stability ranges. (R. B. Sosman, "The Properties of Silica," New York, Chemical Catalog Company, Inc.; Reinhold Publishing Corporation, 1927.)

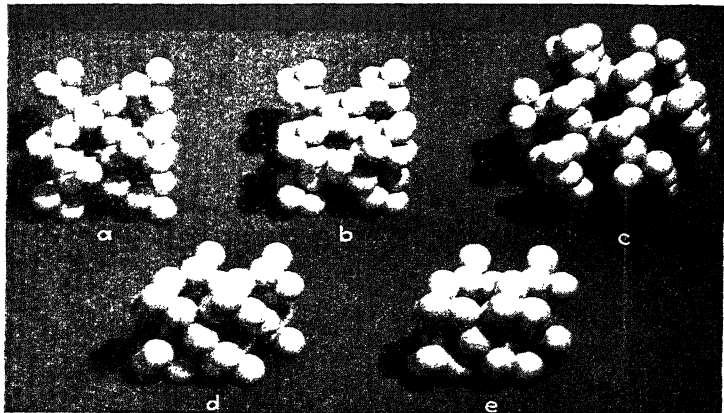


FIG. 142.—Models showing the arrangement of atoms in various polymorphic modifications of silica, SiO_2 . (a) High cristobalite, (b) low cristobalite, (c) high tridymite, (d) high quartz, (e) low quartz. The silicon atoms are not visible because they are small and nestle in a tetrahedron formed by four oxygen atoms. The models do not have similar crystallographic orientations. Note that the low-temperature forms are more closely packed than the high-temperature forms. See page 299 for further discussion.

Quartz can be transformed by heating into a number of polymorphous modifications. These forms, together with their stability ranges, are shown in Fig. 141 taken from Sosman.

There are at least six crystalline varieties of silica: quartz, tridymite, and cristobalite, and each of these has a high- and a

low-temperature modification. All the varieties are characterized by a three-dimensional network of SiO_4 tetrahedrons, each corner being shared with neighboring tetrahedrons. Thus a silicon atom is always shared by two oxygens, which checks the formula SiO_2 , long ago determined by chemical analysis.

Figure 142 shows models that illustrate the manner in which the atoms are arranged in high- and low-temperature cristobalite, high-temperature tridymite, and high- and low-temperature quartz. The silicon atoms nestle in the center of four oxygen atoms and are not visible in this picture. The models are not arranged in a similar crystallographic orientation but rather to show the major features of each structure. One immediately apparent feature is that cristobalite and tridymite are more open packed and have large holes whereas the atoms in high- and low-temperature quartz are tightly packed together and form a close-packed structure free from large holes. Hence, the density and refractive indices of tridymite and cristobalite are very similar, but they differ considerably from those of quartz, as is shown in Table 41.

TABLE 41.—DENSITY OF FORMS OF SILICA
At Room Temperature

	Index of refraction*	Density †	Density ‡
Quartz.....	$\left\{ \begin{array}{l} \epsilon = 1.553 \\ \omega = 1.544 \end{array} \right\}$	2.65	2.653-2.660
Tridymite.....	$\left\{ \begin{array}{l} \alpha = 1.469 \\ \beta = 1.473 \\ \sigma = 1.470 \end{array} \right\}$	2.26	2.28-2.33
Cristobalite.....	1.486	2.32	2.27

* Larsen and Berman, (75a)

† Rogers, (53a)

‡ Dana, (77a)

Quartz is remarkably pure, and consequently the values for its indices of refraction and density are usually very closely alike. There are only meager data on the chemistry of tridymite and cristobalite, but the data that are available indicate that they are usually impure and consequently vary in density and refractive index. On the other hand, it is quite possible that these variations may be due to the little care usually given to the selection of material for such measurements.

In all cases, the high-temperature forms have a higher symmetry than the low-temperature forms. Note that the diagonal groups of tetrahedrons in high-temperature cristobalite form nearly a straight line whereas in low-temperature cristobalite, they form a puckered chain; the same is true in the high- and low-temperature-quartz relationship, although the effect is less apparent in the picture. The differences between the linking of the tetrahedrons in the high- and in the low-temperature forms of each mineral are slight, but they are considerable in quartz, tridymite, and cristobalite. When a high-temperature form is transformed to a low-temperature form, the tetrahedrons are shifted and rotated but none of the links is broken and consequently the high-low transformations of each mineral are rapid and reversible (see Fig. 141):⁵ These inversions are accompanied by volume changes, given in Table 42 below, together with the heat effects that produce them.

TABLE 42.—DENSITY CHANGES ACCOMPANYING INVERSIONS

Form	Density change	Heat effect, g. cal. per g.
Quartz, low-high.....	-0.02	4.5
Cristobalite, low-high	-0.04	5.0
Tridymite, low-lower high...	-0.01	1.0
Idymite, lower high-high...	0.00	

The structures of the minerals quartz, tridymite, and cristobalite are quite different from one another, and the transformation of one to the other requires a marked change in the linking of the tetrahedrons. Consequently, these transformations are extremely slow, and tridymite and cristobalite can exist indefinitely in the metastable state at room temperature. In fact, it is impossible to form quartz from either tridymite or cristobalite by strictly thermal reactions.⁶

The sluggish inversions that are so important to the manufacturers of silica refractories can be greatly influenced by other materials called "mineralizers." A great deal of work has been done on the effect of mineralizers in changing quartz to cristobalite or tridymite in the kiln; and many of these are noted in the references at the end of the chapter.^(51, 60, 61, 62, 64, 72, 73, 74, 75, 85, 87)

The most common one is lime, which is used in most of the commercial silica bricks, partly as a bond and partly as a mineralizer, to hasten the conversion of the quartz to cristobalite and tridymite (Fig. 143). Many other mineralizers have been suggested, such as fluorides, titanium dioxide, boric oxide,



FIG. 143.—Thin section of silica refractory showing a typical wedge-shaped twin crystal of tridymite. There are several less distinct crystals in the field. The surrounding material is cristobalite; 750 diameters, with crossed Nicol prisms and gypsum plate.

ferric chloride,⁽⁷⁶⁾ and sodium chloride. It should be remembered, however, that in commercial production, it is undesirable to cause the inversion to proceed with too great rapidity; for if the volume change proceeds too fast, it will rupture or make unsound the structure of the brick.✓

✓*Kyanite and Associated Minerals.*—Kyanite (triclinic), andalusite (orthorhombic), and sillimanite (orthorhombic) all have the formula Al_2SiO_5 .✓ The structural relations of these minerals

are complex, and for a general discussion the reader should see Bragg.^(32b) On heating, they change over to mullite and glass or to mullite, glass, and cristobalite. The crystalline breakup of these minerals has been thoroughly studied by Greig,⁽³⁸⁾ and the temperature ranges are shown in Table 43 below.

TABLE 43.—DECOMPOSITION TEMPERATURES OF SILICA-ALUMINA MINERALS

Mineral	Kyanite	Andalusite	Sillimanite
Decomposition starts....	1100°C. (2010°F.)	1410°C. (2570°F.)	1550°C. (2820°F.)
Complete decomposition ^a	1410°C. (2570°F.)	1500°C. (2730°F.)	1625°C. (2960°F.)
Peak on thermal curve...	1420°C. (2590°F.)	1510°C. (2750°F.)	1560°C. (2840°F.)
Density before firing....	3.6-3.7	3.1-3.3	3.3

^a This temperature varies with rate of heating and size of grains.

As the density of the mullite is 3.16 and the density of the silica glass and cristobalite is less, it is obvious that there must be an expansion in volume during the conversion. This expansion is particularly evident in the case of kyanite, which has the highest original density, but shows only to a very small extent with the other two minerals. The expansion of kyanite on heating^(30,33,33a) may be a valuable property when combined with clays, as it offsets the shrinkage of the clay. Unfortunately, however, the expansion of the kyanite takes place through a rather small temperature interval, whereas the shrinkage of the clay continues over a much longer range; consequently the two effects do not exactly balance each other. As will be shown later, however, a refractory can be produced that will have exactly the same fired volume as the initial volume. The expansion characteristics of kyanite are dependent a great deal on the size of the grains, a fact that should be taken into account when considering the total expansion.

Topaz.—Topaz, $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$, which has recently been found in some quantity in South Carolina, contains enough alumina to form largely mullite on firing.^(33b) The fluorine accelerates the reaction but is eventually completely driven off together with the water.

magnesite.—The firing properties of magnesite depend largely on its composition. For refractory purposes, a dense, low-porosity material is desired. On heating the raw magnesite, the CO_2 is driven off at temperatures between 400 and 900°C. (750 and 1650°F.), forming immediately the only known form



FIG. 144.—Thin section of Grecian magnesite burned at 1790°C. (3250°F.), which shows the rather typical honeycomb structure of calcined magnesite, and, in addition, small birefringence areas between the boundaries of the small grains. The latter is due to small amount of impurities reacting with the magnesite at high temperatures; 60 diameters, with crossed Nicol prisms and gypsum plate.

of MgO , periclase. At first these crystals are so minute that they can be detected only by means of X rays; but with increasing time and temperature, they grow until they form the usual honeycomb structure shown in Fig. 144. It should be remembered, however, that the periclase crystal is cubic and not hexagonal.

The burned magnesite has a true density of 3.55 to 3.63 and a porosity of 15 to 27 per cent. The greater the impurities present

and the higher the firing temperature the lower the porosity. It is desirable to fire the grain well so that no appreciable shrinkage will occur on firing the brick.

The bond in magnesite refractories is mainly glass, but crystalline material such as forsterite does occur. Iron oxide, in the form of finely divided magnesioferrite, $\text{Mg.Fe}_2\text{O}_4$, occurs to the extent of 7 or 8 per cent in some types of magnesite, which allows the production of a strong and dense product at temperatures very much lower than would be possible with the pure magnesia. Other impurities such as lime, silica, and alumina form glass, which acts as a bond. The burning process is discussed in the references.⁽⁹⁴⁻¹⁰⁹⁾

✓ *Lime*.—Calcium carbonate can be decomposed readily to calcium oxide; and on heating at temperatures as low as 1400°C . (2550°F .), crystals of calcium oxide can be formed. Such crystals are chemically much more stable than the low-calced lime and undoubtedly would serve as an excellent basic refractory if they could be properly protected from moisture.

✓ *Zirconia*.—There are a number of polymorphous modifications of zirconium dioxide; and for a general review the reader should see the papers by Ruff and Ebert,⁽¹¹⁰⁾ Cohn,⁽¹¹⁵⁾ and Clark and Reynolds.⁽¹¹⁶⁾ The natural mineral baddeleyite is monoclinic. Pure monoclinic ZrO_2 , often called the "*C* form," is stable up to 1000°C . (1830°F .) where it is transformed to the *B* form, which is tetragonal; this transformation is reversible. The tetragonal form is transformed irreversibly at 1900°C . (3450°F .) to the A_2 form, which is trigonal. The A_2 form is transformed to the A_1 form, which is also trigonal, at 625°C . (1160°F .), an inversion that is rapid and reversible.

It should be remembered that the inversion temperature and the crystallographic modifications obtained at various temperatures are dependent to a large extent on the composition and impurities that are present. This is again true in the ZrO_2 system. If the nitrate, oxychlorate, oxylate, or certain hydroxides of zirconium are heated, the tetragonal form is obtained at temperatures around 600°C . (1110°F .). This tetragonal form is metastable and is converted to the monoclinic form on further heating. The tetragonal form is also obtained if pure zirconia is heated in the presence of silica at about the same temperature; but whereas the tetragonal form obtained by heating the above-mentioned compounds of zirconium is trans-

formed to the monoclinic form on further heating, the silica-bearing form remains tetragonal up to 1460°C . (2660°F .) where it is transformed to zircon, ZrSiO_4 . If certain oxides such as MgO and CaO are present, a cubic form is obtained at about 1700°C . (3090°F .). This isometric form does not transform on cooling and is obtained only in the presence of the oxide impurities (other types of impurities might act in the same way). Less than 3 per cent magnesia in solid solution will give rise to the isometric form, and the maximum amount of magnesia that exists in solid solution in ZrO_2 is about 28 per cent, which corresponds to the formula $\text{Mg}_2\text{Zr}_3\text{O}_8$.

The most useful compound of zirconium other than the oxide is zirconium silicate, which corresponds to the natural mineral zircon, ZrSiO_4 . This is a stable mineral and can serve as a useful refractory material.

Chromite.—Chromite is the natural spinel-type mineral of theoretical formula FeCr_2O_4 . It is thermally stable and apparently undergoes no polymorphous modifications up to the fusion point. However, the natural mineral always contains impurities in solid solution, such as Ca , Mg , and Al , and admixed mineral impurities such as the silicates. Silica, if in large quantity, is objectionable, as it forms considerable quantities of glass on heating, which lowers the mechanical strength of the chromite refractories at high temperatures. The addition of MgO in the right amount to form the compound forsterite will diminish the amount of glass and provide a superior refractory (see the patents of Seil^(128,134)). Recently, considerable study has been given to bricks of mixtures of magnesite and chromite,^(123,125,126,129,131,132) which have given trouble because of a gradual growth due to absorption of iron oxide. Chrome-silica bricks^(120,121) and chrome-alumina bricks⁽¹²⁴⁾ have been suggested.

TABLE 43a

SiO_2	Quartz	Cristobalite	Tridymite
ZrO_2	Baddeleyite	$\text{B-Zr}_2\text{O}_3$	$\text{A-Zr}_2\text{O}_3$
TiO_2	Brookite	Anatase	Rutile

Titania.—Titanium dioxide also has several modifications and Cohn⁽¹¹⁵⁾ has suggested the interesting analogy between SiO_2 , ZrO_2 , and TiO_2 as shown in Table 43a.

Magnesium Silicate Minerals.—There are a number of minerals of this class such as olivine, talc, and serpentine, which may form the basis of forsterite refractories.^(140,141) In most cases, sufficient magnesite must be added to the natural mineral to convert the low-melting metasilicate to the high-melting orthosilicate. The amount of magnesia added as well as the grain sizes of the various minerals are quite important and are covered by patents such as that of Goldschmidt.^(136,137)

3. Solid Reactions. Importance in Ceramic Processes.—A great many ceramic firing processes take place with little or no liquid phase present; accordingly many believe that the reactions go on entirely between solids. In spite of the great importance of these types of reactions, it was not until recently that a thorough study was made of this phenomenon, although as early as the year 1909, Wright pointed out the fact that calcium oxide crystals would grow rapidly at least 1000°C. (1830°F.) below their fusion point. Most of the recent work in this field has been carried out in Germany by G. Tammann and his coworkers and by Goldschmidt. A very good résumé of the subject is given by Taylor.⁽¹⁵⁶⁾

Mechanism of Solid Reactions.—Solid reactions apparently take place because of loosening of the atomic bonds by thermal agitation, which permits mutual diffusion of the various atoms into the adjacent parts of the structure. The solid reactions can be divided logically into two groups: the first in which we simply grow large crystals from small ones and the second group where we produce a new type of crystal from two dissimilar ones.

The process of diffusion is greatly influenced by many factors in addition to the composition of the original crystals. In the first place, it has been found that the solid reaction progresses much more rapidly at a temperature where one of the crystals involved passes through an inversion point. For example, if a solid reaction is going on between quartz and another mineral, the reaction would be greatly accelerated at a temperature of 573°C. (1063°F.), where the low-temperature quartz changes to the high-temperature form. This is probably due to the loosening of the bonds at the inversion point and permitting of much greater rates of diffusion. It has also been found that gases, such as water vapor and fluorine, act as mineralizers and

greatly accelerate the solid reaction. Again the reactions proceed much more rapidly, as we would expect, when the reacting particles are fine and in intimate contact. It has also been found that the reaction can be accelerated by seeding the mass of reacting crystals with a few fragments of the new crystal to be formed.

One example of solid reaction is the production of periclase crystals of considerable size at temperatures far below the softening point. This is the type of reaction where fine crystals are changed into large crystals of the same kind. Another example is the production of spinel from magnesium oxide and alumina. Here an entirely new crystal is formed, and this can be carried out at temperatures far below the point where any liquid could be formed in the system.

There is some evidence that solid reactions may be caused by the transfer of material in the vapor state, *i.e.*, a kind of sublimation. This is a field needing more study.

4. Firing Properties of Refractory Bodies.—It is seldom desirable to produce a refractory directly from a raw plastic clay because of the large shrinkage and distortion that would occur in firing. A reduction in firing shrinkage is a very desirable accomplishment for the following reasons:

1. It permits the production of a fired refractory that will be close to the desired dimensions.
2. It prevents warping of the refractory on firing.
3. It permits a greater weight of finished bricks to be fired in a given kiln.
4. It makes it unnecessary to control the maximum temperature of firing as carefully as when large shrinkages occur.

Use of Grog.—One of the simplest methods of reducing the firing shrinkage of a refractory is by introducing a nonplastic material, such as grog, an ancient expedient but one that carries a patent history. ^(163, 164, 175, 176, 178, 179, 182) As this material has already been fired and has reached a stable volume, it acts somewhat as a skeleton to hold the brick together in a stable form during the firing operation. Figure 145 shows a curve of firing shrinkage and porosity of a mixture of kaolin and grog burned to a temperature of 3000°F. for 2 hr. The grog was sized for dense packing, bonded with raw Georgia kaolin, and formed in a mold by hand. It is interesting to note that the grog alone has a 3 per cent linear shrinkage when fired at this temperature.

Careful microscopic studies of individual pieces of the same grog fired at the particular temperature showed no volume change and no rounding of the corners; but apparently when the grog is formed into a mass of particles in contact the surface tension or pressure effects are such as to cause rounding of the sharp points and edges sufficient to produce welding and shrinkage.

It is also interesting to note that bond clay can be added up to approximately 25 per cent without any change in the burning shrinkage. As the volume of voids in this grog is approximately 25 per cent of the bulk volume, it will be seen that the

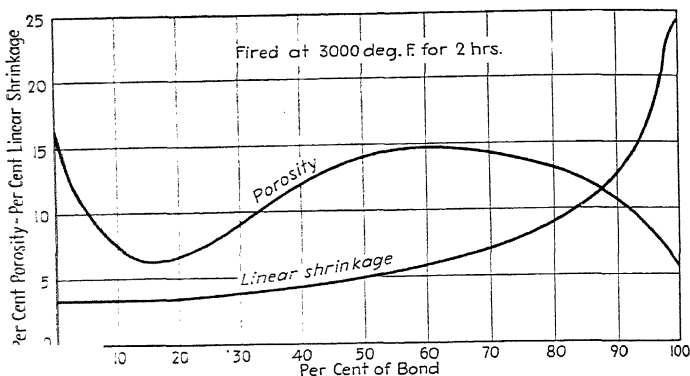


FIG. 145.—Shrinkage and porosity curves. Clay-grog mixtures.

bond is simply acting as a filler in the pore spaces and that when it shrinks, it does not affect the volume of the whole piece, since this is governed by the grog. However, when the amount of bond is increased beyond 25 per cent, the total shrinkage begins to increase more and more rapidly until 100 per cent of bond is reached. This is due to the fact that thicker and thicker films of shrinking bond are built up between the grog grains.

Expanding Minerals.—The shrinkage of a refractory clay can also be controlled by adding a mineral that expands on firing.⁽⁴³⁾ Such a mineral may be kyanite, which, mixed with clay in the raw state or with clay and grog, will give a very definite expansion.

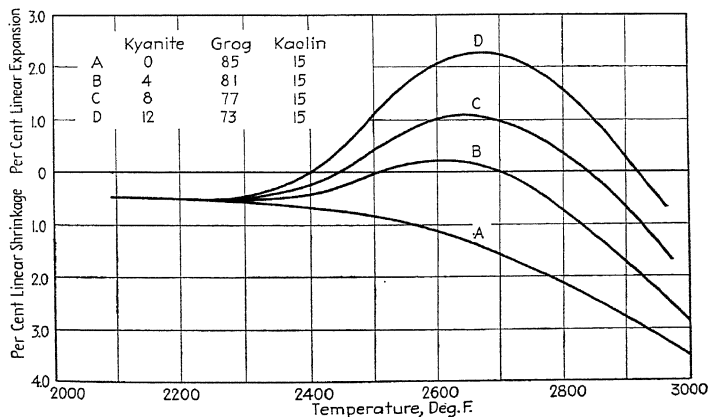
To illustrate this, a few mixes were made by Lane^(92a) using the proportions given in Table 44.

These mixes were molded in a dry press and fired to various temperatures at which they were held for 3 hr. The shrinkage

TABLE 44.—KYANITE-CLAY MIXES ILLUSTRATED IN FIG. 146

Mix	Dense kaolin grog, per cent	Raw N. C. kyanite, per cent	Raw kaolin, per cent
A	85	0	15
B	81	4	15
C	77	8	15
D	73	12	15

Grog sizing		Kyanite sizing	
Screen	Per cent	Screen	Per cent
4-8	35	14-35	50
8-14	15	35-60	30
14-35	6	60-100	10
35-60	4	100	10
60-100	20		
100	20		



✓ FIG. 146.—Expansion caused by kyanite.

curves are shown in Fig. 146. It will be seen that the kyanite gives a real expansion over the range from 2350 to 2600°F.

but beyond this point shrinks faster than the grog and clay mix—a disadvantage when it is attempted to make a refractory to be volume constant at temperatures higher than the original firing. However, the 12 per cent kyanite mixture has the same volume at a firing temperature of 2975°F. as when molded. Kyanite having too coarse grains ruptures and weakens the structure, whereas too fine grains give little or no expansion. Grains of all one size break down over a very small temperature range, giving an undesirable peak in the expansion curve.

The minerals sillimanite and andalusite were also tried out in similar mixtures; and although they showed a small amount of expansion, they were not nearly so effective as the kyanite.

It is theoretically possible to add a high-density mineral like fused alumina to a mixture of grog and bond, which after long heat-treatment will dissolve in the glass and form mullite of lower density. Practically, however, this solution goes on with extreme slowness and seems difficult to carry out in a practical way, although such a method is suggested in a patent of Lambie and Ross.⁽⁴⁴⁾

Bloating.—Reduction of shrinkage can also take place if the clay bloats or forms bubbles in the glass owing to breaking up of sulfides, carbonates, etc. This increase in size by bloating may account for the expansion of some of the high-alumina clays and flint clays in firing, but a great deal more work needs to be done on this question before we will know the exact mechanism causing it. Bloating, if it occurs to any great extent, is not particularly desirable, as it is hard to control and will not occur under any appreciable load. Therefore, a shape being fired may show no change in horizontal dimensions but may shrink materially in a vertical direction.

Molding Conditions.—Shrinkage is also more or less dependent on the conditions of molding, as shown by the curves in Fig. 147 for various water contents and molding pressures of kaolin and water mixtures. In fact, it will be observed that the burning shrinkage is sharply decreased by increasing the water content beyond the critical value of 25 per cent for low molding pressures. Also, the higher the molding pressure the lower is the burning shrinkage. For a given material, a maximum shrinkage in burning can be determined from the density of the dried or partially fired specimen (allowing for ignition loss). This is

shown by the curve in Fig. 148, where the density values are plotted against the maximum linear shrinkage based on the condition of the specimen when the density is determined. This curve applies to both fired and unfired specimens. For example,

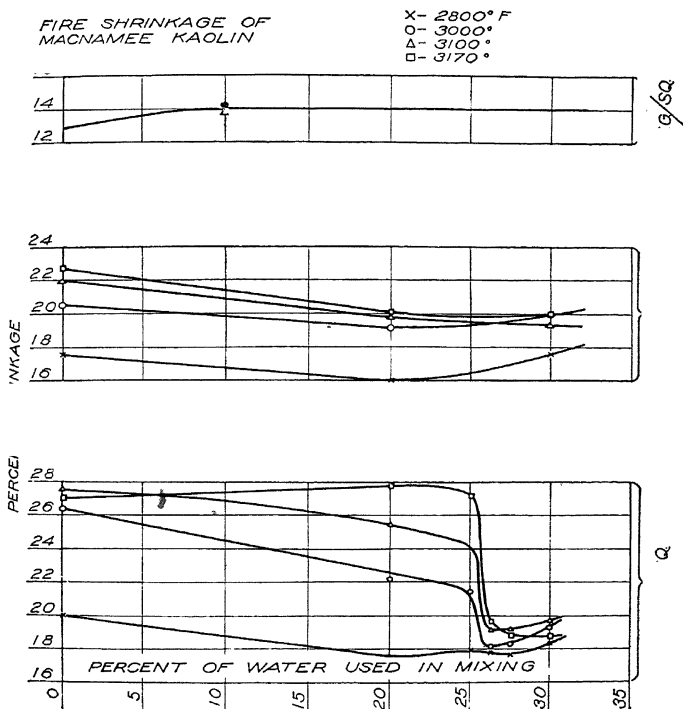


Fig. 147.—Curves showing the burning shrinkage of kaolin for various water contents and molding pressures.

if an unfired specimen has a density of 1.46, it will eventually shrink 22.0 per cent, to the condition of maximum density.

Control of Porosity.—The porosity of a refractory is of great importance, as a low porosity gives better resistance to slag attack and a higher porosity, in general, gives better resistance to spalling. Also, a low-porosity material has a high thermal

conductivity, whereas a high-porosity material such as an insulating brick has a low value. It is important, therefore, that a manufacturer of refractories be able to control the porosity to suit the particular conditions for which the brick is used.

Porosity, in the same way as shrinkage, is controlled to a large extent by the molding conditions; *i.e.*, high pressures in molding give a more densely fired structure. Also, high firing

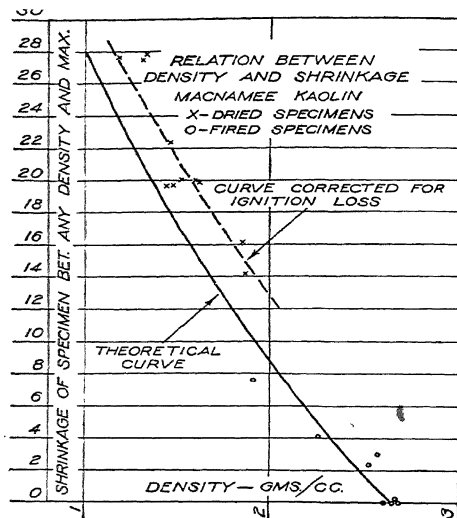


FIG. 148.—Curves showing the relation between density and maximum linear shrinkage for kaolin.

temperatures give low porosities but at the same time are apt to produce distortion.

Perhaps one of the best ways of controlling porosity, especially for producing low-porosity refractories such as glass-tank blocks and slag-resisting brick, is to control the grog size carefully. This is considered so important that many modern refractory plants are controlling the grain size of a grog with great exactness. Much work has been done on the packing of grog particles to produce a structure of the lowest possible density; as noted in Chap. VII. Figure 149 shows the shrinkage and porosity curves

for a densely packed grog body having 15 per cent of clay bond fired at various temperatures.

Chemical Control.—In making certain types of refractories, it is impossible readily to obtain raw materials that are free from a certain objectionable impurity. This impurity can sometimes be converted into a nonobjectionable material by adding a mineral that will combine with it and form a higher fusing compound. An example of this which was briefly mentioned before is the addition of magnesium oxide to chrome ore in such an amount that it will combine with the silica and form the mineral

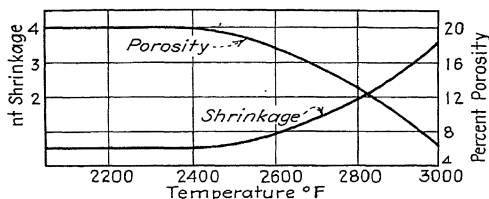


FIG. 149.—Shrinkage and porosity curves for a closely packed grog having 15 per cent bond clay.

forsterite,⁽¹³⁴⁾ the highest melting compound in the magnesia-silica system.

Another example is the production of forsterite refractories, where many of the natural materials, such as olivine, produce excess silica in the form of glass or cristobalite when fired. Magnesium oxide added in the correct amount will combine with the silica to form additional forsterite.

5. Melted and Cast Refractories.—For certain purposes, particularly in the production of glass-tank refractories with a minimum of porosity, it has been found desirable to produce refractories by fusing the raw materials in an electric furnace and pouring the melted refractory into a sand mold to form the desired shape. The melting process itself permits some purification of the raw materials, (1) by the reduction of iron oxide to metallic iron and (2) by the elimination of some of the silica by volatilization or combination with the iron to form ferrosilicon. The casting itself is practically nonporous; and by governing the rate of cooling, the size of the crystals can be regulated as desired. This process, although comparatively expensive,

seems to be justified for producing special refractories, such as mullite and alumina blocks for glass tanks. (184*a*, 185*a*, 186, 187)

6. Specific Heat.—The term “specific heat” has been used in the ceramic literature rather loosely and, in many cases, has been applied not only to specific heat values but to values of latent heat of association, inversion, or crystallization. Specific heat may be defined as a number expressing the ratio of the heat

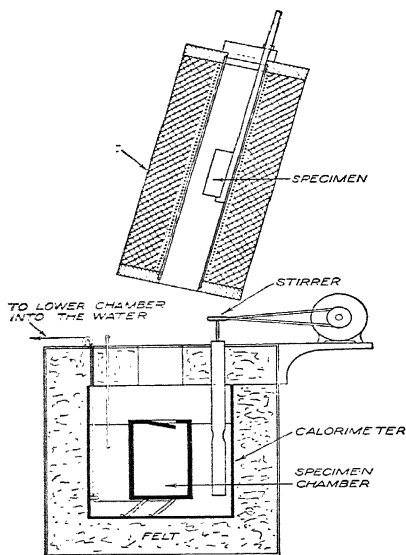


FIG. 150.—Apparatus for measuring specific heat by the calorimeter method.

quantity required to raise, respectively, 1 g. of the given material 1°C. at a definite temperature and 1 g. of water from 19.5 to 20.5°C. Specific heat can correctly refer only to the heat required for raising the temperature of a thermally stable material that is free from any changes through the measured interval. We can, therefore, correctly speak of specific heat as applying to stable refractory materials that have been previously fired to complete all irreversible reactions and that have no reversible changes in the temperature range being measured. For example, the specific heat of quartz is continuous up to 573°C.

(1063°F.), where a crystal change takes place giving off a small amount of latent heat of inversion that must be added to the specific heat to give the total heat content. The use of the term specific heat for raw clays, as is often done, is very unfortunate.

Method of Measurement.—The measurement of specific heat can be carried out with considerable accuracy by the calorimeter method. In this determination, the specimen is heated in a suitable furnace to a known and uniform temperature and then dropped suddenly into a calorimeter which can be immediately immersed in water. The heat content of the specimen is then determined by the rise in temperature of the water and the constants of the apparatus. Equipment for the high-temperature measurements of specific heat is shown in Fig. 150. This apparatus, as used by Wilkes,⁽²⁰⁹⁾ is laid out to give a quick drop of the sample into the specimen chamber with the elimination, necessary for precise work, of splashing and steam losses.

Values.—In Table 45 are given values of specific heat for a considerable number of stable refractory materials. Some of the minerals, such as quartz, cristobalite, and zirconia, have reversible inversions, but these are small in effect and are included by the experimenter in the value for specific heat.

7. Heat Quantity Required to Raise the Temperature of Clays and Ceramic Bodies. *Method of Measurement.*—The determination of the heat required to raise a clay to a certain temperature is a very difficult measurement because the calorimeter method, which can be used for stable materials, is not applicable here. The heat given up on cooling is quite different from the heat absorption in raising the temperature. It is, therefore, necessary to find some way of actually measuring the heat going into a given specimen as it is raised through definite temperature intervals. A number of methods have been used to make these measurements; but because of the inherent difficulties of measuring the heat directly absorbed by the specimen, the results are not highly precise; and a great deal of work is still to be done in this field before we will feel sure of the values.

One of the methods, used for this purpose by Navias,⁽¹⁹⁸⁾ consists in heating the specimen of clay with a surrounding platinum coil which is, in turn, enclosed in a vacuum jacket to prevent possible escape of heat to the outside. Nevertheless, during the rather long period of test, some heat is lost. This is

TABLE 45.—VALUES OF MEAN SPECIFIC HEAT

Material	Temperature range, °C.	heat	Investigators
Alumina, fused.	20-250	0.211	W. Cohn ⁽²⁰⁰⁾
	20-400	0.231	
	20-600	0.231	
	20-800	0.272	
	20-1000	0.304	
Alumina, pure.	30-100	0.206	G. B. Wilkes ⁽²⁰⁹⁾
	30-300	0.226	
	30-500	0.240	
	30-700	0.250	
	30-900	0.258	
	30-1100	0.265	
	30-1300	0.271	
	30-1500	0.276	
Cristobalite.	30-1700	0.280	R. Wietzel ⁽¹⁹⁶⁾
	0-200	0.213	
	0-400	0.242	
	0-800	0.260	
	0-1600	0.276	
Chrome brick.	30-218	0.178	Y. Tadokoro ⁽¹⁹²⁾
	30-318	0.195	
	30-382	0.210	
	30-480	0.216	
	30-579	0.221	
Fireclay brick—35 per cent Al_2O_3	30-894	0.215	Bradshaw and Emery ⁽¹⁹⁴⁾
	25-600	0.228	
	25-1000	0.265	
	25-1200	0.284	
	25-1400	0.297	
Fireclay brick...	600	0.227	J. W. Mellor and others
	1000	0.263	
	1200	0.262	
Fireclay brick.....	200	0.204	E. Heyn and others ⁽¹⁹⁰⁾
	400	0.222	
	600	0.236	
	800	0.248	
	1000	0.256	
Lime, fused..	1200	0.263	P. N. Laschchenko
	375-400	0.181	
	590-680	0.193	
Magnesia, pure.	30-100	0.234	G. B. Wilkes ⁽²⁰²⁾
	30-300	0.247	
	30-500	0.259	
	30-700	0.269	
	30-900	0.277	
	30-1100	0.283	
	30-1300	0.288	
	30-1500	0.291	
Magnesite brick—88 per cent MgO	30-1700	0.294	A. T. Green ⁽¹⁹⁷⁾
	30-1800	0.295	
	25-605	0.265	
	25-825	0.274	
	25-930	0.280	
Mullite, $3Al_2O_3 \cdot 2SiO_2$.	25-1041	0.285	W. Cohn ⁽¹⁹²⁾
	25-1115	0.292	
	20-200	0.161	
	20-400	0.167	
	20-600	0.173	
Porcelain, fired.....	20-800	0.175	W. Cohn ⁽¹⁹²⁾
	20-1000	0.195	
	20-200	0.212	
	20-400	0.232	
	20-600	0.264	
	20-800	0.304	

TABLE 45.—VALUES OF MEAN SPECIFIC HEAT.—(Continued)

Material	Temperature range, °C.	Mean specific heat	Investigators
Quartz glass, SiO_2	{ 0-200 0-400 0-600 0-800 0-1000 0-1200 0-1400 0-1600	0.201	R. Wietzel ⁽¹⁹⁶⁾
		0.223	
		0.239	
		0.251	
		0.258	
		0.262	
		0.269	
Quartz, crystalline, SiO_2	{ 0-200 0-400 0-800 0-1600	0.203	R. Wietzel ⁽¹⁹⁶⁾
		0.223	
		0.259	
		0.271	
Silica brick.....	{ 25-600 25-1000 25-1200 25-1400	0.226	Bradshaw and Emery ⁽¹⁹⁴⁾
		0.263	
		0.282	
		0.293	
Silicon carbide, crystalline, SiC ..	{ 0 200 400 600 800 1000	0.140	O. Weigel ⁽¹⁹¹⁾
		0.233	
		0.277	
		0.275	
		0.225	
		0.129	
Spinel:			
Ferrous aluminate, $\text{FeO} \cdot \text{Al}_2\text{O}_3$..	50-1025	0.25	Parmelee ⁽¹⁴⁴⁾
Magnesium aluminate, $\text{MgO} \cdot \text{Al}_2\text{O}_3$	50-1025	0.29	Parmelee ⁽¹⁴⁴⁾
Magnesium aluminate, $\text{MgO} \cdot \text{Al}_2\text{O}_3$	{ 0-243 0-399 0-534 0-632 0-783 0-886 0-1042	0.214	A. E. MacGee ⁽²⁰²⁾
		0.229	
		0.232	
		0.250	
		0.255	
		0.257	
Zinc aluminate, $\text{Zr} \cdot \text{Al}_2\text{O}_3$	50-1025	0.22	Parmelee ⁽¹⁴⁴⁾
Ferrous chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$..	50-1025	0.20	Parmelee ⁽¹⁴⁴⁾
Magnesium chromite, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$	50-1025	0.22	Parmelee ⁽¹⁴⁴⁾
Manganese chromite, $\text{MnO} \cdot \text{Cr}_2\text{O}_3$	50-1025	0.18	Parmelee ⁽¹⁴⁴⁾
Zinc chromite, $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$	50-1025	0.18	Parmelee ⁽¹⁴⁴⁾
Ferrous ferrite, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$	50-1025	0.20	Parmelee ⁽¹⁴⁴⁾
Magnesium ferrite, $\text{MgO} \cdot \text{Fe}_2\text{O}_3$	50-1025	0.20	Parmelee ⁽¹⁴⁴⁾
Manganese ferrite, $\text{Mn} \cdot \text{Fe}_2\text{O}_3$	50-1025	0.21	Parmelee ⁽¹⁴⁴⁾
Zinc ferrite, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$	50-1025	0.17	Parmelee ⁽¹⁴⁴⁾
Zirconia—99 per cent, ZrO_2	{ 25-600 25-1000 25-1200 25-1400	0.137	Bradshaw and Emery ⁽¹⁹⁴⁾
		0.157	
		0.167	
		0.175	

measured by immersing the vacuum jacket in a water bath, which permits the heat escaping to be measured. By calibrating this apparatus with a material of known specific heat, the proportion of heat going into the sample and the proportion going into the container, coil, etc., can be calculated. A test is then made by heating the given sample to a certain temperature and holding it there until equilibrium is reached, the heat input being measured by the number of watts supplied to the heater. The

TABLE 46.—THE HEAT REQUIRED TO BURN UNFIRED BODIES

Material	Temperature, °C.	Cal.* to heat 1 g. from 20° to t°C.	Investigators
Ball clay (Kentucky).....	0-200	68	A. E. MacGee ⁽²⁰¹⁾
	0-400	159	
	0-600	285	
	0-800	366	
	0-1000	465	
Diaspore clay.....	0-200	70	A. E. MacGee ⁽²⁰¹⁾
	0-400	150	
	0-600	274	
	0-800	350	
	0-1000	450	
Firebrick body.....	0-200	68	A. E. MacGee ⁽²⁰¹⁾
	0-400	145	
	0-600	268	
	0-800	337	
	0-1000	415	
	0-1200	507	
Fire clay, raw Chamotte.....	200	35	W. Cohn ⁽¹⁹²⁾
	400	80	
	600	201	
	800	243	
	1000	326	
	1200	452	
	1400	572	
Kaolin, Georgia.....	0-200	79	A. E. MacGee ⁽²⁰¹⁾
	0-400	183	
	0-600	332	
	0-800	402	
	0-1000	496	
Kaolin, Zettlitz.....	200	37	W. Cohn ⁽¹⁹²⁾
	400	86	
	600	241	
	800	333	
	1000	420	
	1200	489	
	1400	560	
Porcelain body (green).....	200	34	W. Cohn ⁽¹⁹²⁾
	400	81	
	600	193	
	800	248	
	1000	331	
	1200	428	
	1400	528	
* In the cases noted the initial temperature is 0°C.			

temperature is again raised to another level; the additional heat input measured; and so on. From these values, a curve of heat input against temperature can be plotted.

White⁽¹⁹³⁾ and Cohn⁽²⁰⁰⁾ supported a specimen of the clay in a small container in the center of a wire-wound furnace and determined the heat passing from the furnace wall to the specimen by the temperature difference between the specimen and the furnace. By calibrating this apparatus with a specimen of known specific heat, the heat input for any given specimen can be computed.

MacGee⁽²⁰¹⁾ used a differential thermal method in which a specimen of the clay and a specimen of a neutral substance of known specific heat were placed side by side in a wire-wound furnace. A differential thermocouple recorded the difference in temperature between the two specimens, from which the heat input to the clay sample through any temperature interval could be computed.

Perhaps one of the most satisfactory methods, but one that has not as yet been applied extensively to clays, is that suggested by Smith,⁽²¹²⁾ in which a comparatively thick-walled refractory crucible is placed in the center of a wire-wound furnace with the clay sample inside it. A differential thermocouple with the junctions respectively on the inside and the outside surface of the crucible is connected to a temperature controller which raises the furnace at such a rate that a definite temperature difference is always present in the walls of the crucible. The heat input to the sample is always constant for given time intervals, assuming no change in conductivity with small temperature changes. Therefore, a plot of furnace temperature against time will enable a curve of heat input against temperature to be established. It should be noted that unlike the other methods, calibration factors are not necessary, provided the thermal conductivity of the crucible wall is known.

In Table 46 will be found values for the heat required to raise various types of clays and ceramic bodies to definite temperature levels.

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CHAPTER X

KILNS FOR BURNING REFRACTORIES

We know that kilns have been used by man for many thousands of years, as their remains are frequently found in the excavations of ancient sites of early civilization. These primitive kilns were of the updraft type and, in most cases, consisted only of a firing chamber, a perforated floor, and a wall. The con-



FIG. 151.—A Chinese kiln with a number of sections. It is lighted at the bottom, the waste gases preheating the higher chambers, and the cooling of the lower chambers preheating the combustion air. The fuel is small chips of dry wood fed through the holes in the crown. (*Henry Jewett Greene.*)

struction of a permanent kiln roof was too much of a structural problem for most of the early potters, and recourse was made to a temporary roof of green poles and raw clay which would hold in place long enough for the very low temperature of firing used at that time. There is, however, one exception, as a kiln has recently been found in Tepe Gawra that was believed to have had a permanent roof at a period as early as 4500 to 4000 B.C.

The early Chinese kilns, which consisted of a series of chambers extending up the side of a hill, were remarkably similar to our modern chamber kilns and permitted a considerable degree of control as the fire advanced from one chamber to another. An interesting kiln of this type is shown in Fig. 151.

It should be remembered that in dealing with these early kilns as well as our modern ones, four essentials must always be present: (1) a means for producing the heat, (2) a support for the ware, (3) a container such as the walls and crown to confine the

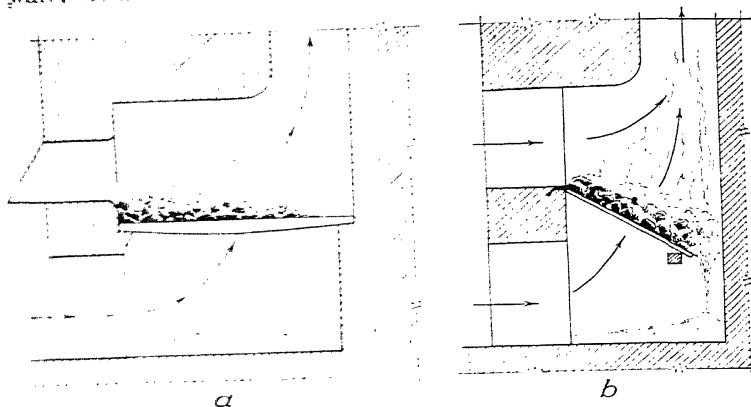


FIG. 152. Kiln furnaces with flat and sloping grates.

heat in the working space, and (4) a means to transfer the heat from the source to the ware.

1. General Principles. *Production of Heat.*—As the majority of refractories are fired with coal as a fuel, this method of heating will be discussed first. Coal is used because of its low cost and because most of the refractories are not particularly sensitive to impurities in the kiln gases that might arise from using coal as a fuel. The coal is generally burned in furnaces with sloping or flat grates as shown in Fig. 152. The air for combustion passes partly through the fuel bed and partly over the top, the hot gases generally going upward into the kiln over a bag wall, as shown in Fig. 153. In the round or rectangular kilns, a considerable number of furnaces are spaced around the wall of the kiln in order to distribute the heat as evenly as possible.

The manufacturers of refractories generally prefer for their kilns a good grade of bituminous coal giving a long flame; also a low ash content and a high fusion point of the ash is desirable. In most cases, it is necessary to have a low sulfur content so that sulfates will not deposit on the surface of the bricks during the water smoking period.

It is the general practice to fire the coal by hand, although mechanical stokers have been tried in a few instances. The great

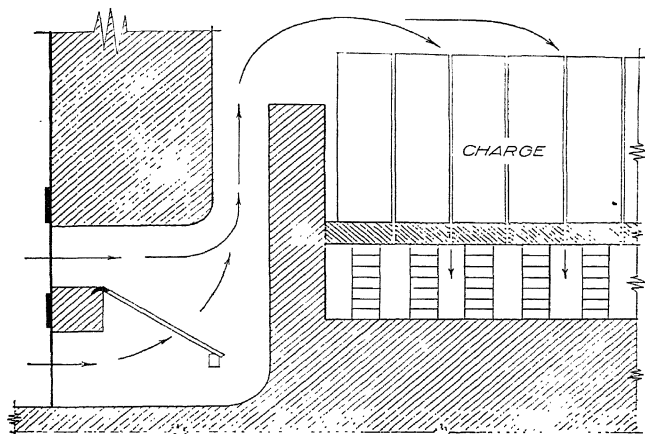


FIG. 153.—Passage of gases through a downdraft kiln.

difficulty with the mechanical stoker lies in the fact that the firing is distributed into so many small units that the stoker has not been particularly successful, although it is true that a uniform firing would be more economical than the intermittent firing necessary with hand operation. ✓

Many of the coal-fired kilns waste a good deal of heat as a result of radiation from the more or less open fire mouths and escaping gases from the fire bed which are not pulled into the kiln by the draft. These conditions have been improved in some of the modern installations by tighter doors and forced draft. ✓

Oil has many advantages as a fuel for firing refractories; and in some localities, the cost compares favorably with coal.

Advantages of oil are a more perfect temperature control, the possibility of a higher maximum temperature, a generally cleaner kiln atmosphere, and a smaller labor requirement for the firing operation. Oil is, of course, obtainable in a number of different grades; but from the cost standpoint, the heavier grades of oil, such as Bunker C, are generally used. A number of different types of burner are available for firing with oil. In principle, they all break the oil up into a spray of fine particles and inti-

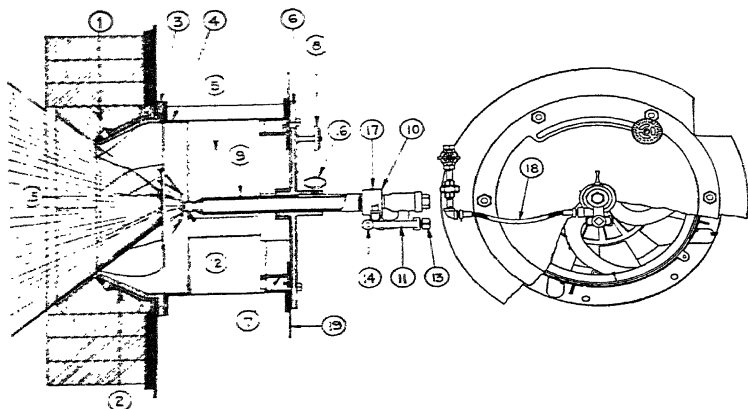


FIG. 154.—A mechanical atomizing burner. (Courtesy of Babcock and Wilcox Company.)

ately mix them with the combustion air. In burners of the mechanical atomizing type, as shown in Fig. 154, the oil is atomized by forcing it through a fine orifice at relatively high pressure. This method is particularly suitable for burners of high capacity, as the orifice becomes very tiny for small burners and there is apt to be danger of particles getting through the filter and plugging the orifice.

Oil is also fired in air- or steam-atomizing burners where high-pressure air or steam is used to inject the oil into the kiln and at the same time break it up into a fine mist. Secondary air is generally supplied from a low-pressure source. A burner of this type is shown in Fig. 155. In setting up an oil-burning system, care should be taken that it be properly laid out to

ensure reliable operation. The heavier oils have to be heated and must be kept hot until they actually reach the burner; otherwise the viscosity will become so great that proper atomization is impossible. A good filter that will permit cleaning without shutting down the oil flow is necessary, and often a complete recirculating system is desirable. In Fig. 156 is shown a layout for an oil-fired kiln that has been found quite satisfactory.

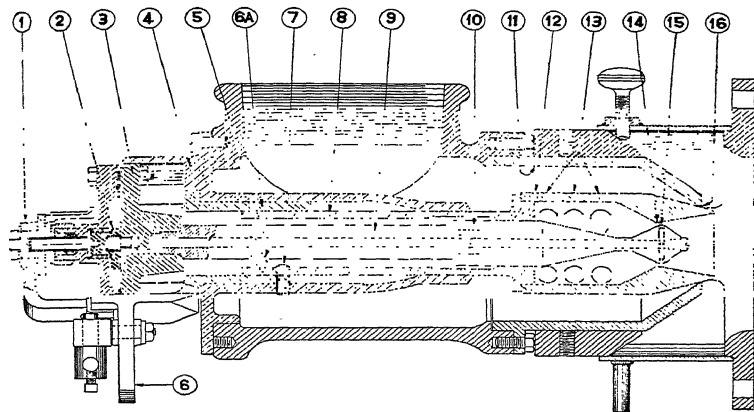
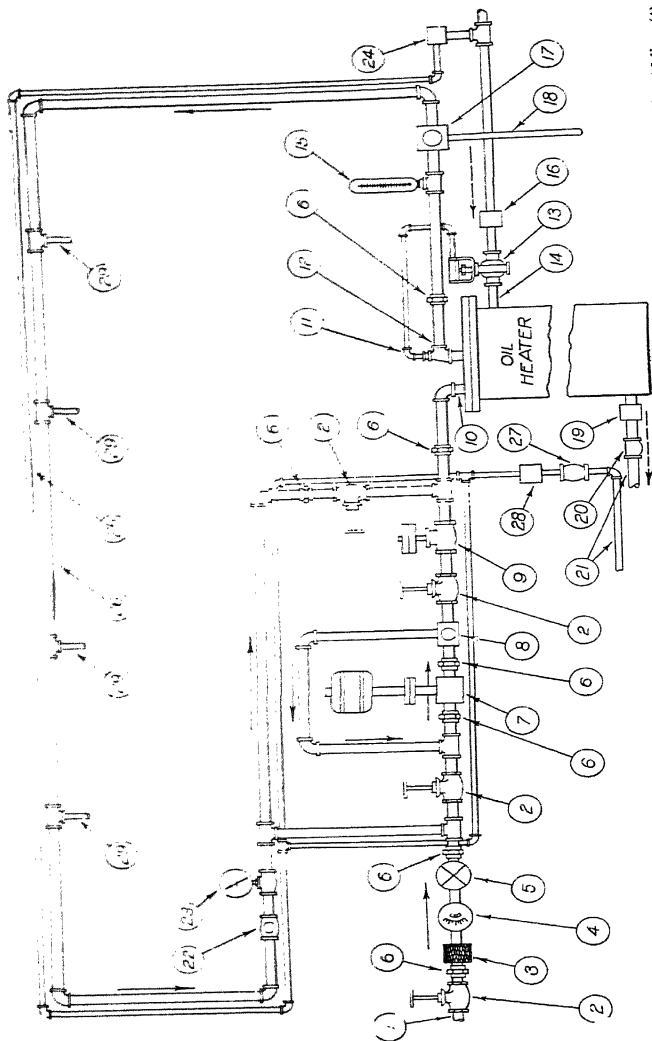


Fig. 155.—An air-atomizing oil burner. (1) Oil-control valve lever. (2) Oil-control valve cam. (3) Oil-control valve consisting of a V-groove in a flat surface. (4) Burner backplate. (5) Curved slot. (6) Operating lever. (7) Inner-nozzle operating pin. (8) Inner air-nozzle operating tube. (9) Oil tube. (10) Oil nozzle. (11) Outer air nozzle. (12) Inner air nozzle. (13) Primary air-supply openings. (14) Primary air discharge. (15) Oil nozzle. (16) Secondary air-discharge opening. (*Courtesy of Hauck Manufacturing Company.*)

In regard to the arrangement of the burners in the kiln, they may fire over the charge in a downdraft kiln, as shown in Fig. 157; or they may fire against the side of the charge, preferably through a checker brick to distribute the heat, as shown in Fig. 158. In setting up the burner, care must be taken to allow sufficient combustion space for the particular burner used; otherwise carbon will tend to build up on the surfaces around the flame. The recommendations of the burner manufacturers should be followed when the combustion chamber is laid out.

[illegible]

Natural gas is an excellent fuel for burning refractories, but in only a few localities is it sufficiently plentiful to make its use economical. It has the advantage of making temperature con-

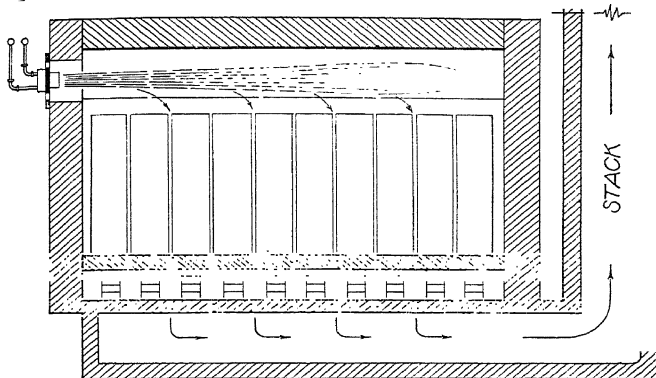


Fig. 157.—An oil-fired kiln in which the flame passes above the charge.

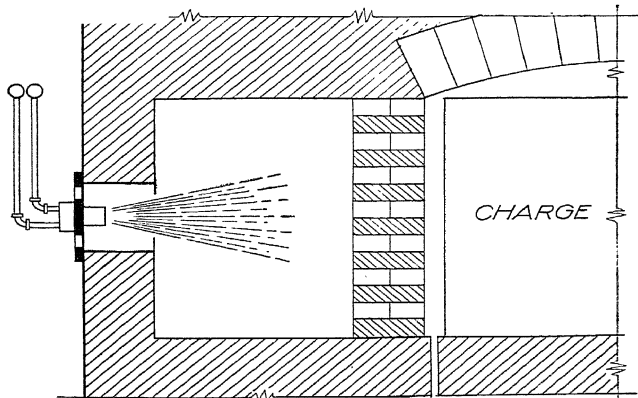


Fig. 158.—A kiln in which the oil flame passes through a checkerwork.

trol a simple problem, and the heat produced is very clean. In general, the burner cost for a gas installation will be found less than that for burning oil. ✓

Producer gas is used to some extent in firing kilns. In most cases, the gas is used hot and without scrubbing; consequently

provision must be made for draining and cleaning the connecting pipes between the producer and the burner, as they periodically fill up with tar and soot. In regions where only low-grade coal is available, the producer-gas firing is found to be quite successful. The producer gas gives a comparatively low-temperature flame, so there is little danger of overheating any part of the charge; and as the volume of gas is large because of this low heat value, it tends to give an even temperature throughout the kiln. The small-unit gas producer has been steadily improved and is a much more reliable and efficient piece of equipment than it was in the past.

TABLE 47.—PROPERTIES OF TYPICAL COMBUSTION GAS AT ATMOSPHERIC PRESSURE

Temperature		Relative volume	Specific heat at constant pressure	Viscosity, poises
°C.	°F.			
0	32	1.0	0.22	170 × 10 ⁻⁶
100	212	1.3	0.22	220
200	392	1.7	0.23	260
300	572	2.0	0.24	290
400	752	2.3	0.25	320
500	932	2.8	0.25	350
600	1112	3.1	0.26	370
700	1292	3.4	0.26	390
800	1472	3.8	0.27	410
900	1652	4.2	0.27	430
1000	1832	4.6	0.28	450
1100	2012	4.9	0.28	460
1200	2192	5.3	0.29	480
1300	2372	5.7	0.30	490
1400	2552	6.1	0.30	500
1500	2732	6.5	0.31	510
1600	2912	6.8	0.32	510
1700	3092	7.2	0.33	520
1800	3272	7.5	0.34	520
1900	3452	7.9	0.35	530
2000	3632	8.3	0.36	530

There is not space here to go into the principles of combustion, but it should be remembered that the amount of excess air used is of the greatest importance in all kiln firing. The greatest combustion efficiency is reached with very low amounts of excess

air; but on the other hand, a large volume flow of gases is needed to carry out the moisture in the water-smoking stage of firing, to provide uniformity of temperature, and to supply enough oxygen to burn away carbonaceous matter. Some of the properties of a typical combustion gas are shown in Table 47.

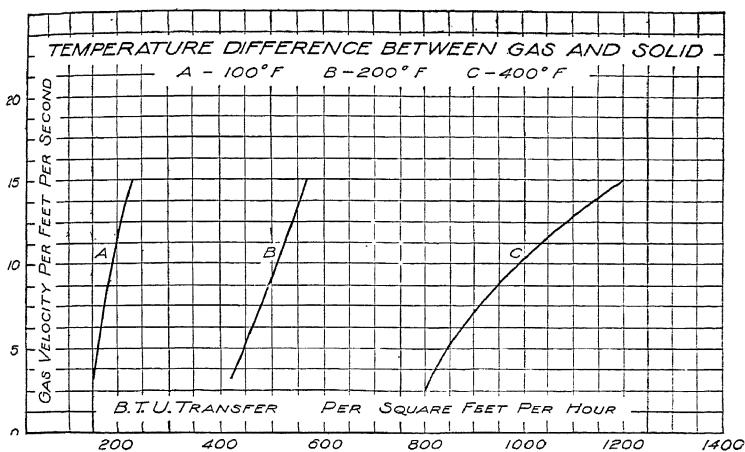


Fig. 159.—Rate of heat transfer between a gas and a solid.

Because of its high cost, electric heating is not used to any extent for firing refractories. An exception to this is the firing of small pieces, such as spark-plug porcelains.

Transfer of Heat.—One of the most difficult problems in kiln design is to transfer the heat efficiently from its source to the ware. The problem is unusually difficult in the kiln because the ware is in small units stacked into a considerable volume and therefore radiant-heat transfer, so important in furnaces such as those used in the metallurgical industry, can play little part. For the same reason, conduction of heat into a bulky charge of small units is of little consequence. Therefore, we must rely almost entirely upon convection for heating of the charge.

The transfer of heat from a moving stream of gas to a solid surface is well understood. The transfer rate depends mainly on the temperature difference between the gas and solid and the

velocity with which the gas is passing by the solid. The curves in Fig. 159 give an idea of the rate of heat transfer under different conditions between a gas and a solid. The transfer of heat from the moving gas by radiation from the gas itself and the incandescent particles that it contains is quite important in furnaces of

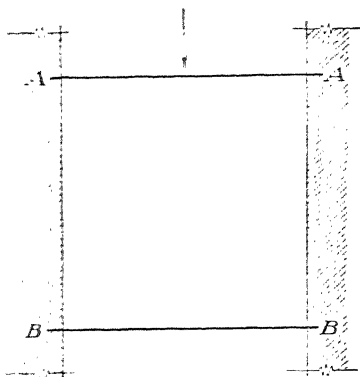


FIG. 159. The effect of flow velocity on temperature distribution.

large volume and great flame thickness, such as would be found in the glass-tank or open-hearth furnace; however, in the kiln, where the gas stream is divided into relatively thin layers, this radiation cannot play a very important part, although attempts are made in practice to use long-flame coal to bring the heat down to the bottom of the charge of a downdraft kiln.

Equalization of Temperature.

One of the most important problems in kiln design is to produce a uniform temperature throughout the volume of the charge. This is by no means an easy matter, as few large periodic kilns now operating show a difference of less than 50°F. from top to bottom of the charge. In tunnel kilns, with their small cross section, the temperature uniformity is better, but here again it is apt to vary from place to place in the car by an appreciable amount.

Considering first the case of a downdraft kiln under equilibrium conditions, it may be readily shown that the temperature difference between top and bottom is related to the mass flow of gases. In Fig. 160, the section *AA* may represent the top of the charge and *BB* the bottom. If *M* equals the weight of gases flowing through the channel in a unit time, and *S* the heat lost between *AA* and *BB* by transfer laterally through the walls per unit time, then

$$S = (t_1 - t_2)c_p M,$$

$$(t_1 - t_2) = \frac{S}{c_p M}$$

where c_p = the specific heat of the gas

t_1 and t_2 = the temperatures of AA and BB , respectively.

We may therefore conclude that a more even temperature is obtained by a large volume flow, which may be realized by the addition of excess air to the products of combustion. This equation also shows that insulation of the kiln side walls will give a more even vertical temperature distribution. ✓

✓Another method of equalizing the temperature and one that is theoretically very attractive is the recirculation of the combustion gases through the charge. In this way, a large volume flow is obtained, thus decreasing the temperature difference; while at the same time, the volume of gases leaving the kiln is relatively small. The only difficulty with the recirculation method is the practical problem of handling the high-temperature gases. At the lower temperatures encountered in heat-treating furnaces, gases can be recirculated with water-cooled, alloy fans at temperatures close to 1800°F. (about 980°C.); but above this, the only possible means is by injector action, a method quite successful in driers but one that has not been developed for kilns at the present time. Recently, recirculation has been used successfully in some tunnel kilns. ✓

• The equalization of temperature at right angles to the path of flow is readily accomplished by adjustments in the floor openings, so that the hotter areas have the openings reduced and the cooler areas have them enlarged. By trial and error, a very uniform temperature can be attained over the horizontal cross section of the charge. ✓

• One often hears the kiln fireman state that he uses a damper or a close-set floor to back up the heat in the kiln and give a more uniform temperature. It is not generally understood, however, just what the effect of dampers and restrictions to the flow accomplish. The curves in Fig. 159 show clearly the great increase in heat transfer from the gas to the charge with increasing velocities. ✓The point in the kiln where the flow is restricted has an increased velocity, and thereby more heat is transferred from the gas to the charge. As the usual problem is to raise the temperature at the bottom of the charge, it is possible to have a relatively open setting in the charge itself and as small floor openings as are permitted by the available draft. Owing to the high velocity through the floor openings, the heat from the gas

will be given up to a much greater extent at the floor than in the other parts of the charge and will therefore tend to compensate for the gradual cooling of the gas as it goes down through the charge.

Temperature uniformity can be attained in a muffle kiln by varying the area of contact of the gas with the muffle wall⁽⁷⁾ from the burner to the exit point; *i.e.*, at the burner, the passage for the gas would only have a small width in contact with the muffle, whereas in the exit, it would have a large width. By properly adjusting these areas, a muffle kiln with absolute uniformity of temperature can be constructed. Laboratory kilns that have been made in this way, although bottom fired, show a temperature at the top of the muffle within a few degrees of the bottom temperature.

Insulation of the kiln tends to increase the uniformity of inside temperature, because (1) it tends to keep the inside walls of the kiln at a more uniform temperature, and because (2) an insulated kiln requires less fuel and therefore the gases entering the kiln can be at a lower temperature. Also, as explained from the diagram in Fig. 160, the insulation of the walls of the kiln increases the uniformity of temperature by minimizing the heat loss as the gases pass through the charge.

Kiln Efficiency.—The efficiency of the kiln is usually defined as the ratio of the heat required to bring up the ware to its maximum temperature divided by the amount of heat supplied by the fuel. This definition is perfectly logical when applied to the periodic kiln; but when it is used under conditions where recuperation occurs, then it may become absurd, as efficiencies of over 100 per cent have been determined on actual kilns. This can perhaps be made clear by the set of heat-balance diagrams shown in Fig. 161 beginning with a nonrecuperative kiln and ending with one having a high recuperative effect. It will be seen that the heat required to bring the ware up to temperature is the same in each case but that the external heat supplied to the kiln becomes progressively smaller as the recuperative action increases. It would seem more reasonable to give fuel consumption per thousand standard-sized bricks rather than to express efficiency in percentage.

It should be stated here that a high degree of kiln efficiency is often incompatible with good uniformity of temperature

because high efficiency demands a low temperature of exit gases and these, in turn, mean a low temperature of the charge in the bottom of the kiln. Only by recuperative action or recirculation can good temperature uniformity be obtained together with high efficiency.

It is obvious that the insulation of kilns will increase their efficiency; but unfortunately very little data are at hand to

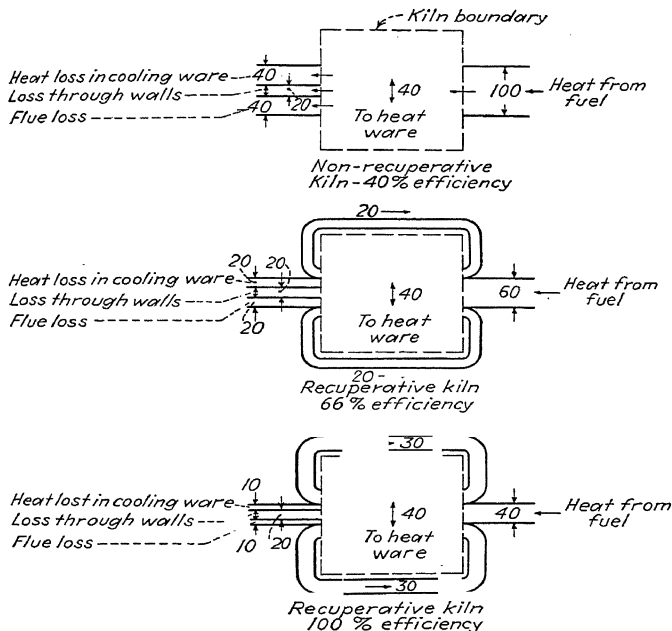


FIG. 161.—Heat balance diagrams.

show just what the saving might be, as there is seldom an opportunity to compare similar kilns, one of which is insulated and the other not. It should be brought out, however, that the effect of insulation is not only to reduce the heat passing through the walls and the crown of the kiln but also to reduce the volume of exit gases in proportion. This fact is little understood, and it may be well to emphasize it with an example, under steady temperature conditions, in Table 48.

This follows because, for a constant exit temperature, the heat lost in the flue gases is proportional to the heat input.

TABLE 48.—SAVING DUE TO INSULATION

	Uninsulated kiln	Insulated kiln	
		As usually computed	As it occurs
Heat passing through walls, B.t.u.	50,000	25,000	25,000
Heat lost in flue gases, B.t.u.	50,000	50,000	25,000
Heat supplied to the kiln, B.t.u.	100,000	75,000	50,000
Heat saved, per cent.	0	25	50

2. Laboratory Kilns.—The only practical fuel to use in small laboratory kilns is natural or manufactured gas. Although oil can be used in the larger types of laboratory kilns, the control of

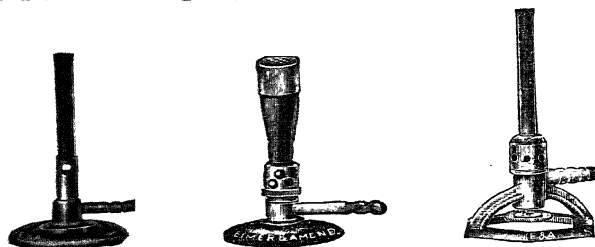


FIG. 162.—The Bunsen, Meker, and Tirill types of atmospheric gas burners.
(Courtesy of Eimer and Amend.)

the temperature and the ease of operation in the small ones are not entirely satisfactory, owing to the fact that oil requires for complete combustion a considerable amount of space and time, which is not usually available in the operation of most laboratory kilns.

Types of Gas Burners.—There are a number of types of burners suitable for the efficient combustion of gas. The simplest is the atmospheric type, where the primary air is drawn in by the gas jet. Examples of this are the Bunsen-, Tirill-, and Meker-type burners, as shown in Fig. 162. With gas at the usual pressure of 3 to 6 in. of water, it is impossible to draw in enough primary air for complete combustion; consequently a certain amount of secondary air must be supplied in addition. With

natural gas, which requires a larger proportion of air, the primary air is quite insufficient for combustion; therefore it is much more difficult to design an efficient burner of this type to burn natural gas. However, by proper design, furnace temperatures as high as 1420°C . (2588°F .) can be obtained with atmospheric burners without preheating the air. If the air is preheated, temperatures as high as 1750°C . (3182°F .) may be obtained. The advantages of the atmospheric type of burner are quietness and reliability, for a burner of this type can be left running unattended quite safely.

Although it is possible to preheat the air for small kilns successfully, fuel saving is usually not an object in such small

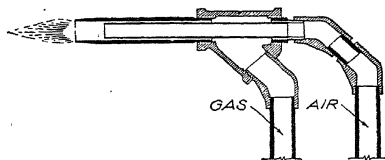


FIG. 163.—A blow pipe where the gas and air are mixed at the nozzle.

installations, and the initial cost and maintenance of a suitable recuperator is not often justified; accordingly, when temperatures above the range of the atmospheric burner are desired, it is best to use the air or gas under pressure. By supplying the gas at a comparatively high pressure with a small pump, sufficient primary air can be drawn in to give complete combustion. Under the conditions of complete combustion at the top of the burner, a much higher temperature can be obtained than when secondary air must be supplied separately. The high-pressure-gas type of burner has the advantage of a very large range of control from the lowest to the highest temperatures. The greatest disadvantage is the special apparatus that must be used for compressing the gas.

Perhaps the most common types of gas burners used in laboratory kilns are the ones to which the air is supplied under pressures of from 2 to 12 lb. per sq. in. The gas and air are mixed at the nozzle somewhat as shown in Fig. 163, and a fairly short flame results. Temperatures as high as 1600°C . (about 3000°F .) can be obtained with this type of burner. In controlling the heat of the furnace, two adjustments must be made—one on the gas

and one on the air—but this has the advantage of allowing the kiln atmosphere to be regulated as desired.

The highest temperatures in laboratory kilns can probably be obtained by premixing the gas and air in the theoretically correct proportions and then burning them at the nozzle, as shown in Fig. 164. Under proper conditions, temperatures up to 1850°C . (about 3360°F .) can be obtained without preheating. The high temperature is due to the fact that the gas and air are

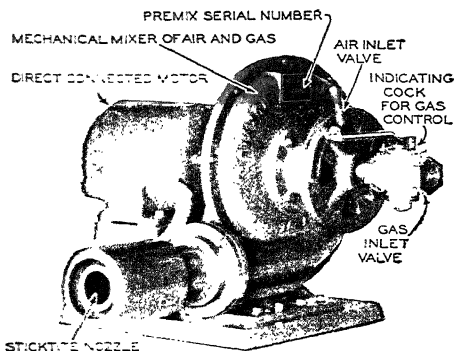


Fig. 164.—A gas burner in which the air and gas are premixed and then burned at the nozzle. (Courtesy of Mazon Premix Burner Company.)

intimately mixed before combustion and that the combustion itself occurs extremely rapidly in a very small volume.

Small High-temperature Kiln.—In Fig. 165 is shown a drawing of a small kiln for obtaining very high temperatures in a volume large enough to contain several full-size bricks. In this case, the gases are premixed, are introduced through a tuyère near the top of the kiln, and pass down through the floor and then up through four stacks. The temperature distribution over the floor can be equalized by partially closing off one or more of the stacks. There is a considerable temperature gradient between the top and bottom of the charge in this kiln, because the charge is heated to a considerable extent by radiation. Under favorable conditions, temperatures as high as 1850°C . (about 3360°F .) can be attained without preheating.

Small Round Kiln for Shrinkage Tests, etc.—Figure 166 shows a small furnace that is very convenient for heating small

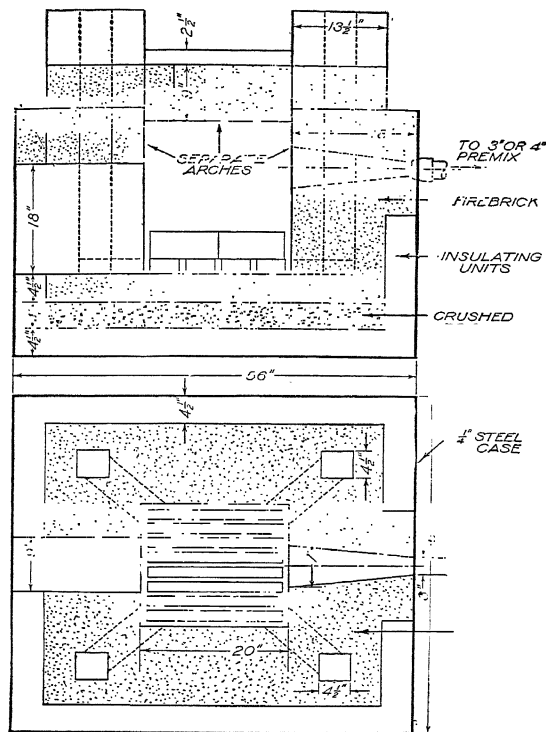


FIG. 165.—A small gas-fired kiln.

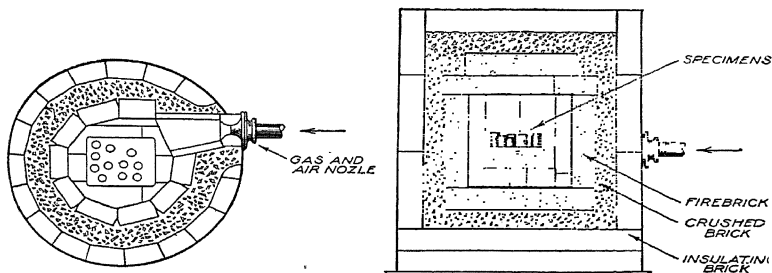


FIG. 166.—A gas furnace for temperatures up to 1800°C.

specimens. By placing the specimens in open saggars, a very even temperature is attained because of the complete circulation of the gases around the specimens. The use of premixed air and gas gives temperatures up to 1800°C . (about 3270°F .).

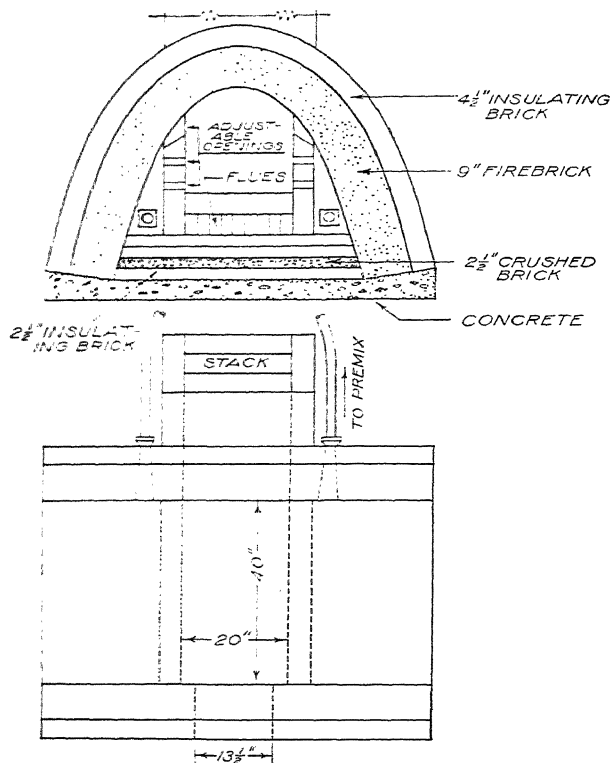


FIG. 167.—A small kiln designed to give an even temperature distribution.

Kiln for a Uniform Temperature.—In Fig. 167 is shown a somewhat larger kiln designed to give an even distribution of temperature. The gases from the burners pass into two chambers, from which they escape to the charge through adjustable openings in the bag walls. They then pass down through

the charge and out through the flues. Owing to limitations in the permanency of the bag walls, the temperature in this type of kiln is limited to perhaps 1700°C. (about 3090°F.). It is very satisfactory for burning trial batches of bricks on any desired schedule.

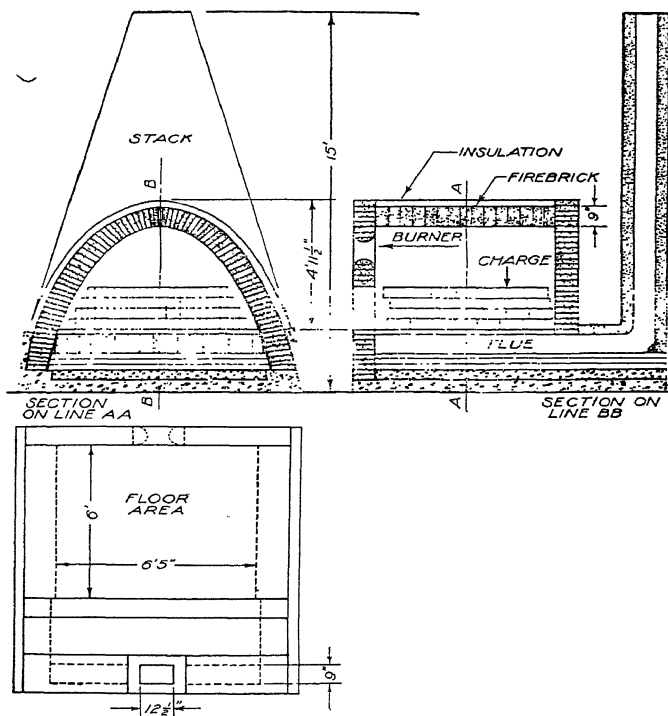


FIG. 168.—A laboratory kiln for burning 100 to 500 bricks.

Large Laboratory Kiln.—There is shown in Fig. 168 a drawing of a laboratory kiln of sufficient size to burn 100 to 500 standard-size bricks. This size of kiln is very convenient for making burns on experimental bricks or special shapes, where the schedule is different from that of the production kilns. The kiln can be fired by either gas or oil, and temperatures up to 1750°C. (about

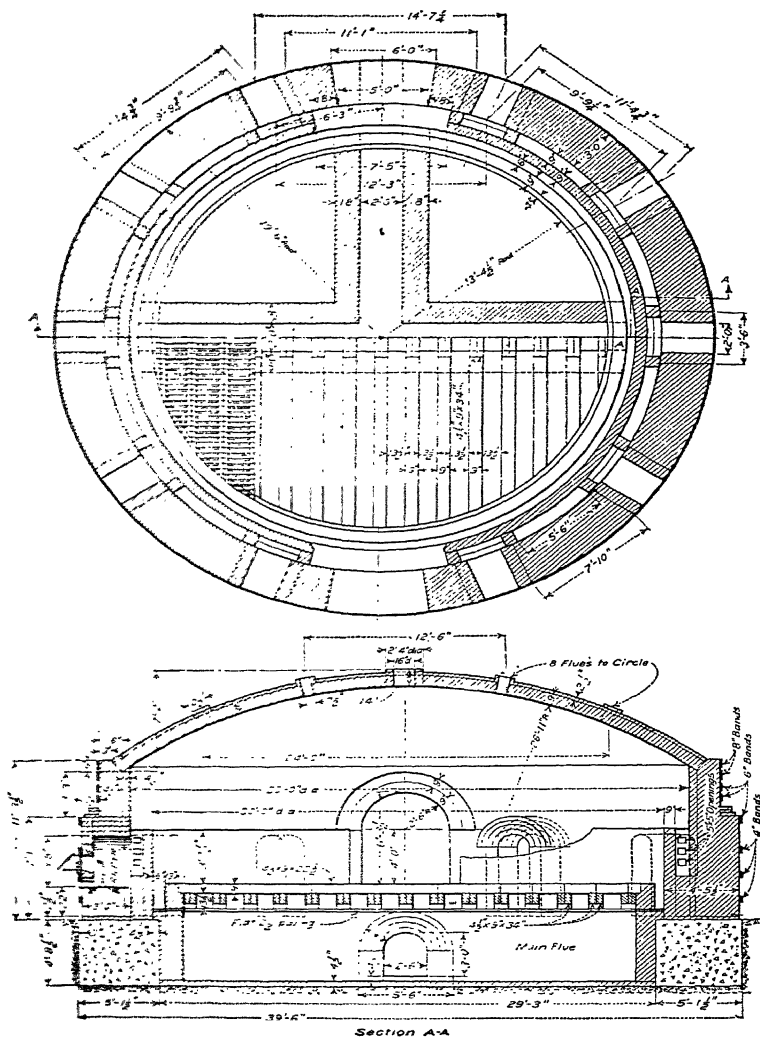


FIG. 169.—A round downdraft kiln for firing refractories. (*J. Am. Ceram. Soc.*)

3180°F.) can be obtained. The temperature distribution can be made quite uniform by varying the floor openings. It will be noted that the elimination of the side walls on this kiln greatly simplifies the construction and makes it unnecessary to use much ironwork.

3. Periodic Kilns.—The periodic kiln has been much used in the refractories industry. Its advantages are a comparatively low first cost and flexibility in operation. The disadvantages are the poor fuel economy secured, the unevenness of temperature when the charge is piled high, and the strain on the brickwork due to the repeated heating and cooling. Although the periodic kiln is being gradually displaced by the tunnel kiln, it will always be used to some extent for burning large shapes and special bricks.

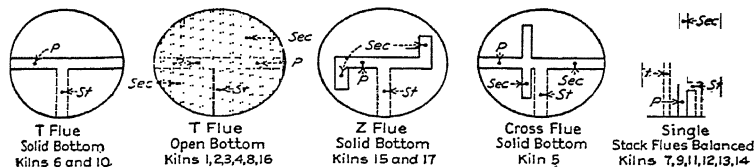


FIG. 170.—Flue arrangements for downdraft kilns.

Common Types of Kilns.—The periodic kiln generally used to fire refractories is either of the circular downdraft type or of the rectangular type. The former is generally preferred because of the low cost for a given capacity and the even temperature distribution possible. The round kilns are made in sizes of from 26 to 42 ft. inside diameter, but sizes from 30 to 36 ft. are generally preferred. The capacity ranges from 30,000 to 140,000 nine-inch equivalents. The fireboxes are arranged around the kiln and vary in number from 8 to 18 according to the size and type. The construction of the walls and crown is practically the same in all cases; but there is a great diversity of arrangements for the floor and flues.

In Fig. 169 is shown a well-designed, round, downdraft kiln for burning refractories. It will be noted that the flues are arranged in such a way as to give an even draft at all parts of the floor. Figure 170 gives a number of other flue arrangements that are sometimes used.

Although there is considerable variation in the dimensions of this type of kiln, the figures in Table 49 are generally used.

It is generally considered good practice to connect two or four kilns to a single stack having separate flues for each kiln. This method gives a hot stack under all conditions, so that a good draft is produced when starting a kiln. The height of stack generally varies from 30 to 40 ft.

TABLE 49.—KILN AREAS

Floor to top of crown, ft.....	11 - 19
Height of bag wall above floor, ft.....	3 - 5
Area of floor openings, per cent of floor area.....	2.8-10
Area of grates, per cent of floor area.....	8 - 12.6
Area of main flue, per cent of floor area.....	1.4- 3
Area of stack, per cent of floor area.....	1 - 1.6

Usually the turnover time in this type of kiln, burning clay refractories, is approximately 14 days: $4\frac{1}{2}$ days for firing,

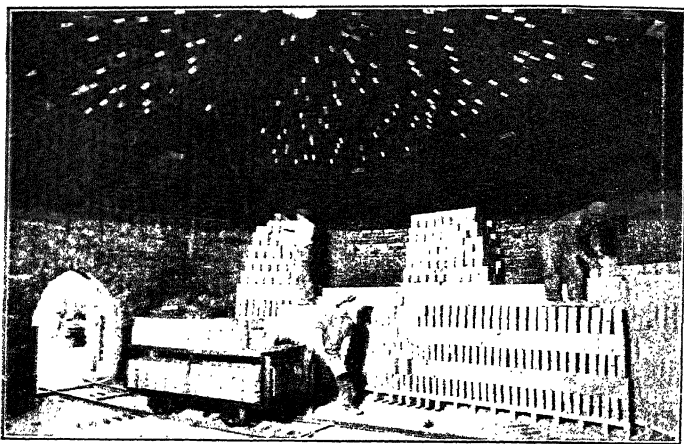


FIG. 171.—A typical kiln setting. (Courtesy of Harbison-Walker Refractories Company.)

$5\frac{1}{2}$ days for cooling, 2 days for drawing, and 2 days for setting. When burning silica brick, the kiln is held at the maximum temperature for some length of time, so the turnover time is somewhat longer. A typical kiln setting is shown in Fig. 171.

The modern tendency seems to be toward the use of blowers and suction fans to accelerate the burning and cooling. In this

way, as much as 50 per cent can be taken off the burning and cooling time, which means a marked increase in the output of the kiln. There is, however, a limit to the rate of firing, caused by the burning properties of the clay used. On the other hand, the cooling rate is limited because of the strains set up in the kiln itself by a too rapid change in temperature.

There are a number of other types of periodic kilns for burning refractories, but they are not so generally used. Descriptions of them can be found in the references given at the end of this chapter.

Fuel Consumption.—The fuel consumption of periodic kilns is comparatively large and varies with the burning temperature and the amount of insulation used on the kiln. In Table 50 are given some figures on the fuel used in a number of periodic kilns.

TABLE 50.—FUEL CONSUMPTION OF PERIODIC KILNS

Type of kiln	Capacity, 9-in. equivalents	Fuel	Maximum temperature		Firing time, hr.	Fuel per 1,000 bricks (9-in. equivalents)
			°C.	°F.		
Round downdraft.....	{	65,000 Coal	1270	2318	192	2,200 lb.
		32,000 Coal	1290	2350	150	1,450 lb.
		60,000 Coal	1320	2408	156	1,200 lb.
		48,000 Coal	1170	2138	132	1,500 lb.
		Coal		2600		3,000 lb.
Round downdraft.....	{	Coal	1150	2100		2,100 lb.
		Coal	1250	2280		2,500 lb.
		Coal		2400		2,400 lb.
Rectangular downdraft...	{	42,000 Coal	1280	2336	163	1,770 lb.
		60,000 Coal	1270	2318	168	1,800 lb.
Round downdraft.....	{	76,000 Oil	1270	2318	110	125 gal.
		Oil	1400	2550		115 gal.
Rectangular (insulated) downdraft.....	{	10,000 Oil	1650	3000	115	400 gal.
		5,000 Oil	1650	3000	100	500 gal.
Round downdraft.....	50,000	Natural gas	1250	2280	216	18,000 cu. ft.

The heat losses in periodic kilns are mainly in the flue gases, as shown in the following table which gives average figures for periodic kilns burning fireclay bricks with coal.

Setting Methods.—The method of setting the brick in the periodic kiln depends on their shape, the type of refractory, and individual plant practice. The setting is usually in a

TABLE 51.—HEAT BALANCE OF A TYPICAL PERIODIC KILN
Per Cent

Heat to raise temperature of bricks, or efficiency.....	15-45
Heat to drive off moisture.....	0-3
Heat in combustion of ash.....	4-10
Heat in combustion in flue gases.....	0-5
Heat in dry flue gases.....	20-45
Heat in water vapor in gases.....	4-7
Heat to raise temperature of kiln walls.....	4-15
Heat to raise temperature of kiln crown.....	2-4
Heat lost by walls and crown.....	3-9
Heat lost in bottom and flues.....	4-12

checkerwork pattern, with about $1\frac{1}{2}$ in. between bricks, making up a bench extending across the kiln. For straight bricks, this means three set across three others. To prevent the bricks

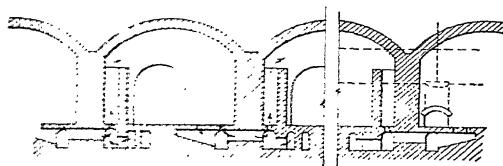


FIG. 172.—Section of a typical compartment kiln.

from sticking to one another, silica sand is sprinkled on the top of the bench before placing the next pieces. Brick such as magnesite and chrome cannot support themselves in a high setting and therefore are commonly boxed with silica brick, which carry the load.

4. Continuous Compartment Kilns.—The compartment kiln is designed to provide more economical operation than can be given by the periodic kiln. A great number of methods are used, but the general principle is the same in all cases. In Fig. 172 is shown a portion of a typical compartment kiln. Each chamber is similar to a downdraft periodic kiln; but instead of the gases passing out of the stack, they pass from one chamber to the bag wall of the next, so that the heat from the combustion gases is used to preheat the bricks in the chambers ahead of the fire. In the same way, the heat from the cooling bricks is used

to preheat the air for combustion. In some cases, this combustion air is drawn off by blowers and passed through the grates or burners; in other cases, the fuel, usually in the form of fine coal, is introduced through ports directly into the chambers under fire.

This type of kiln has been used to a very small extent for refractories in this country, but abroad, where economy of fuel is more important, the compartment kiln has been extensively employed. The main trouble with the older type of chamber kiln was the slow rate of fire travel, which amounted to only about 6 in. per hr. This was due mainly to the considerable resistance to the flow of gases through the long passages. In the more modern chamber kilns, blowers and suction fans are being used to increase the gas velocity, which gives a fire travel as high as 3 to 5 ft. per hr., with an immense increase in the capacity of a given kiln.

In a well-designed chamber kiln, practically the only heat loss is by transfer through the walls and crown, for heat is abstracted from the cooling bricks and from the combustion gases. Although it is difficult to get strictly comparable figures, it may be said that the fuel consumption runs between one-half and one-third of that of a periodic kiln. This, of course, is an important saving. However, the initial cost for chamber kilns is somewhat higher than for periodic kilns of the same capacity; and in general, the firing of a chamber kiln requires more skill to produce an evenly burned product. In regard to the upkeep of the chamber kiln, different operators hold rather conflicting views, but some believe it to be considerably higher than for a periodic kiln.

TABLE 52.—FUEL CONSUMPTION OF CHAMBER KILNS

Type of kiln	Fuel	Maximum temperature		Fuel per 1,000 bricks, lb.
		°C.	°F.	
Continuous chamber.....	Producer gas	1420	2588	1500 (coal)
Continuous chamber.....	Direct coal	1410	2570	1100

✓ The capacity of chamber kilns depends entirely upon the size and number of chambers, as well as rate of fire travel.

Kilns with an output of over 100,000 bricks per day have been constructed.

5. Tunnel Kilns.—The use of tunnel kilns in burning refractories is extending rapidly, and it may be said that practically all the modern refractory plant units are built around a tunnel kiln. As the design has been improved and experience gained in the operation of tunnel kilns, it is generally recognized that they will produce better bricks at a lower cost than the periodic-kiln unit. This does not mean that the periodic kiln will not be used, for it still offers advantages in burning large or intricate shapes where the burning schedule must be different from that of the standard brick. Because of the great importance of the tunnel kiln, considerable space will be devoted to a consideration of the principles of operation.

In principle, the tunnel kiln consists of an elongated chamber, which is maintained at a steady temperature graded in the desired manner from end to end. The charge, mounted on cars, is moved continuously through the chamber and encounters in its passage the desired variations in heat. The economy of the tunnel kiln is obtained by regaining the heat from the combustion gases to heat the incoming charge and by using the heat from the cooling bricks to preheat the combustion air or, in some cases, to dry the bricks.

The advantages of the tunnel kiln are as follows:

1. The tunnel kiln lends itself well to a continuous production process, which minimizes handling.
2. The setting and drawing of the kiln are simple and regular; and with dry-pressed brick, setting can be done directly from the press, eliminating shods, drier cars, etc.
3. The kiln structure itself is always at a uniform temperature, so with proper design, upkeep of the refractory of the kiln itself is very low.
4. It is possible by proper design to heat and cool the ware according to any desired schedule, which enables the brick to be burned properly in the shortest possible time.
5. Owing to the relatively small cross section of the charge, the heat is able to penetrate to the center rapidly, thus allowing much more rapid burning than is possible in the bulky charge of the periodic kiln. This rapid burning is an advantage when special orders must be put through rapidly.

6. The tunnel kiln, when properly operated, shows marked economy of fuel in comparison with the periodic kiln.

There are a number of disadvantages to the tunnel kiln, but many of these are gradually being eliminated as more experience is gained with this method of burning.

1. The construction of a tunnel kiln necessitates a considerable capital outlay, as it is impossible to increase the capacity gradually as can be done with a number of periodic kilns. However, the cost per thousand bricks produced is not necessarily higher than that with the periodic kiln.

2. A shutdown on a tunnel kiln is serious, as it will tie up the whole unit for perhaps two to four weeks. With proper operation, a shutdown is very rare, but it does happen occasionally.

3. The upkeep on the car tops is high, because of the fact that they are periodically heated and cooled during each passage through the kiln. Considerable study is being given the problem, and it seems probable that this expense can be greatly reduced by careful design.

4. Some difficulty is experienced in getting a uniform temperature across the section of the tunnel kiln. The top and sides of the charge are often hotter than the bottom. This can be corrected, however, for some tunnel kilns now running give a very uniform temperature distribution.

5. The tunnel kiln requires a considerable length of floor space, and some plants are so situated that this is not readily available.

6. Another objection to the tunnel kiln is that for most efficient operation, it must be run with a uniform charge, *i.e.*, with straight bricks or 9-in. shapes. It is, of course, possible to vary the burning schedule to accommodate larger shapes or different types of clay, but these changes have a bad effect on the structure of the kiln, and some time is lost in getting the kiln running uniformly after such a change is made.

7. The tunnel kiln cannot be run efficiently at a low capacity and therefore lacks the flexibility of the periodic kiln.

Tunnel kilns are made in the direct-fired and muffle types. Because the average refractory is not very sensitive to impurities in the atmosphere, the muffle type, which is more expensive in first cost and in fuel, would rarely be selected for burning refractories; therefore we shall confine ourselves to the direct-fired type. In Fig. 173 is shown a plan section of a typical direct-

fired tunnel kiln. The charge enters the kiln at the left-hand end and is gradually heated, reaching a maximum temperature

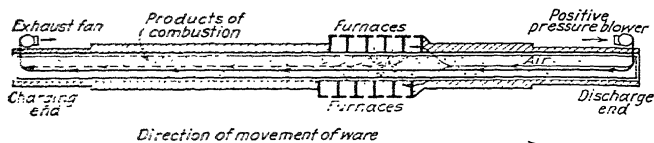


FIG. 173.—A plan section of a direct-fired tunnel kiln. (American Refractories Institute.)

in the hot zone. It is then cooled as it passes out of the kiln. Cold air is forced into the exit end of the kiln with a blower, and this passes through the charge, cooling it and at the same

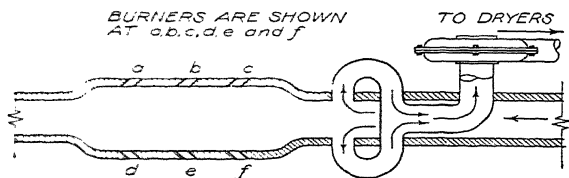


FIG. 174.—Tunnel kiln in which the cooling air is drawn out for use in drier.

time picking up heat. This air then passes into the combustion zone, where it is mixed with the combustion gases, and then passes through the incoming charge. In this portion of the kiln, it loses heat to the charge; then it is drawn out at the entrance end of the kiln with a suction fan. The primary air used for combustion in the burners is usually drawn out from the cooling section by a fan, but this is small in volume compared with the total gas flow.

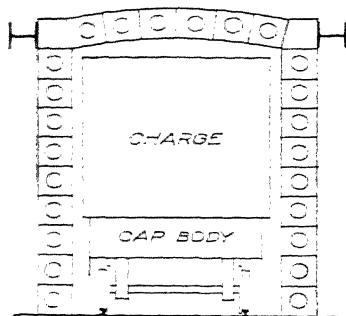


FIG. 175.—A tunnel kiln with indirect cooling.

used for heating driers or a hot floor, and the air for combustion is taken from the cooling air at the same point. Figure 175 shows a kiln with indirect cooling. In this case, the bricks are

cooled entirely by radiation, as the cooling air passes through the hollow walls and is used for driers and combustion.

In order to regulate the heating curve of the bricks, the gases are usually not drawn off at one point at the kiln entrance but are taken out at a number of points along the preheating section so that the desired temperature curve may be obtained.

The longer the preheating zone of the kiln the cooler will be the exit gases and the higher the efficiency of the kiln. However, for constructional reasons, the length must be limited; consequently the temperature of the exit gases usually runs between 100°C. (212°F.) and 400°C. (about 750°F.). In the same way, the outgoing bricks may be cooled to any desired temperature by sufficient length of the cooling zone. It is generally desired to cool the charge sufficiently for easy handling. The bricks usually emerge at temperatures of 50°C. (about 120°F.) to 150°C. (about 300°F.).

The setting of the charge itself should be so proportioned that a comparatively high gas velocity is maintained throughout the length of the preheating zone; and yet excessive power should not be required to pull the desired volume of gases through. In general, the velocity of the gases through the preheating zone will vary from 500 to 2,000 ft. per min., and the draft at the entrance end needed to supply this velocity will vary from $\frac{1}{4}$ to 1 in. of water.

A great many methods are used in setting the charge to provide longitudinal gas channels. As the sides of the charge have a tendency to heat before the center, it is common practice to provide a gas channel down the center of the charge and to reduce the clearance at the top and sides to a minimum, as shown in Fig. 176. The width of the charge usually ranges from 4 to 7 ft., and the height from 4 to 6 ft. Rather flat arches are used in order to prevent gas from flowing over the charge. It is quite necessary in a kiln of this length to make the sections as airtight as possible. This is accomplished by keeping the wall joints well cemented; and in some cases, airtight coatings are applied to the outside of the insulating material.

There would tend to be a very large leakage between the car bottom and the kiln wall, because the clearance here cannot be made small on account of the change in dimensions of the car top. This leakage is prevented in most kilns by attaching to each

car a blade that runs in a trough filled with sand along each side of the kiln, as shown in Fig. 177. This method appears to be

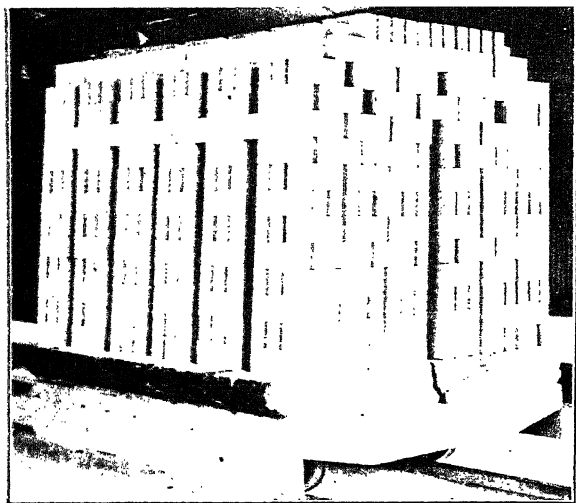


Fig. 176.—Tunnel kiln car loaded with brick. The central gas channel is shown. (Courtesy of A. P. Green Fire Brick Company.)

quite satisfactory, as sand can be supplied to the entrance end of the trough from which it is gradually carried through to the exit end, where it can be removed and returned.

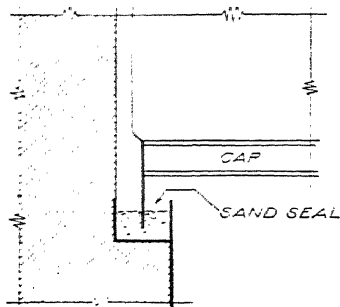


Fig. 177.—A sand seal under a tunnel kiln car.

may be designed to work at their maximum efficiency with a

constant load. Although a number of kilns have been fired directly with coal, in general it is more difficult to maintain a uniform temperature, and better control is obtained with other fuels. Many tunnel kilns are fired with oil. In most cases, the burners are placed in small chambers at the side of the firing zone, and the oil flame is directed into the charge. Due to the

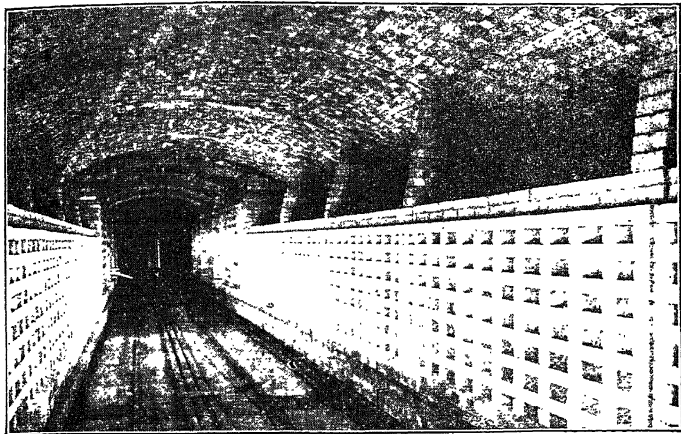


FIG. 178.—Firing zone of a tunnel kiln showing the checkerwork in front of the burners. (Courtesy of Robertson and Company, Inc.)

necessarily small distance between the burner and the charge, there is danger of overheating the surface of the brick next to the burner. For this reason, a checkerwork, as shown in Fig. 178, is sometimes placed at the mouth of the chamber to distribute the heat more evenly over the surface of the charge.

Kilns fired with natural gas need only a small firing chamber, as the flame is comparatively short. As in the case of periodic kilns, natural gas is an ideal fuel and perfect control of temperature and atmosphere can be maintained with it.

Producer gas is often used in firing tunnel kilns. In most cases, the flame can be directed immediately into the charge because of the low temperature of the producer-gas flame. Because of the low heat value of this gas, it is not necessary to use a large amount of secondary air to provide a sufficient volume of gases to

carry the heat down the kiln. As previously stated, raw producer gas has the disadvantage of depositing soot and tar in the connecting flues, and provision must be made for cleaning them out periodically.

The position of the burners is usually somewhat below the center of the charge in order to bring up the bottom temperature, which tends to lag behind that of the top. Sometimes burners in the hot zone are varied in height from one point to another

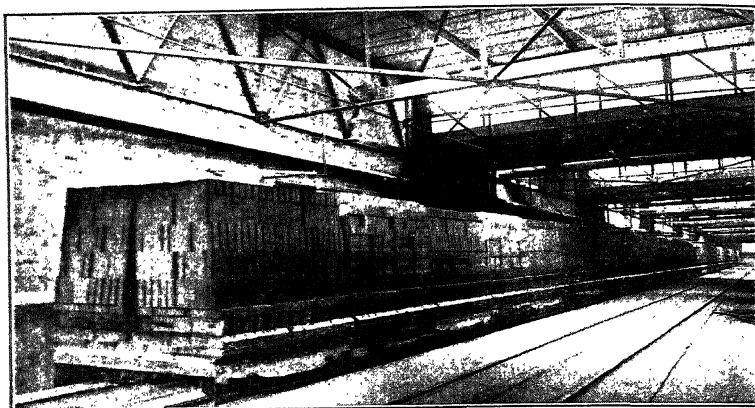


FIG. 179.—Hollow car bottoms. (*Courtesy of Harbison-Walker Refractories Company.*)

in order to give a more equal temperature distribution to the charge. Some kilns have been constructed with hollow car bottoms, as shown in Fig. 179. In this case, the car tops must be made of excellent material to withstand the high temperatures and loads experienced under these conditions.

The tunnel kiln cars vary from 5 to 7 ft. in length and are built of structural steel or made of castings. Generally the cars roll on wheels mounted on roller bearings as in track cars. The track, however, is laid with great care, and there is little side clearance between the flanges and the rails. A number of other methods have been suggested and tried out for supporting the cars, such as balls running in grooves, floats on a canal, and stationary rollers in the kiln.

The cars are pushed through the kiln generally by a hydraulic pusher operated by a small variable stroke pump; as shown in Fig. 180. After one car has been pushed in, the plunger draws back, a second car is inserted by means of a cross transfer, and the process is repeated. At the exit end, the car is taken off on a transfer in the same way. Kilns have been built where the cars are moved continuously rather than intermittently, in which case, they are usually driven by a heavy chain with dogs. Means are provided to transfer the load gradually from the

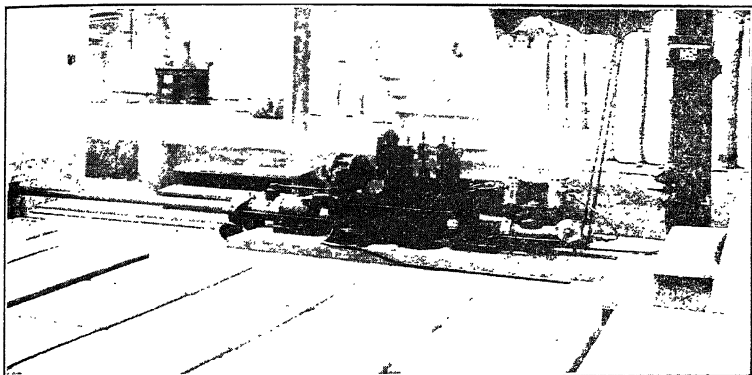


FIG. 180.—A hydraulic car pusher. (Courtesy of Robertson and Company, Inc.)

driving dog on the forward car to that on the following car to prevent shock and jars. As it is more expensive to construct a mechanism for continuous operation, it is not generally used, because the wait of four or five minutes while changing cars is not serious.

Nearly all tunnel kilns employ air locks at both ends so that the flow conditions in the kiln will not be disturbed by the entrance or exit of cars. However, kilns can be run, with one lock and, in the smaller sizes, without any.

The cars are moved at the rate of from 3 to 8 ft. per hr., depending upon the length of kiln and the burning properties of the clay, thus giving a total time in the kiln of from 50 to 100 hr.; however, kilns are operating successfully at speeds as high as 20 ft. per hr. and with a total time in the kiln of 12 hr. If the

kiln is properly designed so that the combustion gases are evenly distributed around each brick, the limit in rate of heating for many clays is the time taken for the heat to penetrate from the surface to the center of the brick. In the future, we may see clay refractories burned in a much shorter time than is considered possible at present.

The production of tunnel kilns generally used for refractories varies between 20,000 and 35,000 bricks per day. It may be said that the faster the bricks can be run through a given kiln and still be burned properly the more efficient will be the burning

TABLE 53.—THE FUEL CONSUMPTION OF TUNNEL KILNS

Type of refractory fired	Fuel used	Maximum temperature		Fuel per 1,000 bricks
		°C.	°F.	
Fireclay.....	Coal	1270	2320	700 lb.
		1335	2435	900 lb.
		1470	2680	1,250 lb. (stokers)
Fireclay.....	Oil	1400	2550	80 gal.
		1670	3040	130 gal.
		1150	2100	850 lb. (coal)
Fireclay.....	Producer gas	1250	2280	970 lb. (coal)
		1420	2590	1,150 lb. (coal)
		1400	2552	630 lb. (coal)
Fireclay.....	Natural gas	1140	2080	6,000 cu. ft.
		1100	2000	7,000 cu. ft.
Chrome.....	Oil	1470	2680	500 gal.
		1525	2775	600 gal.

conditions. It takes but little more fuel to burn 30,000 bricks per day in a given kiln than it does 20,000 bricks.

Some manufacturers burn all shapes in their tunnel kilns, even up to 45 in. in length. They also change the burning temperature to accommodate different types of clay which may be run through the kiln. Although this procedure can undoubtedly be followed if necessary, a tunnel kiln can be run efficiently only with one type of setting and one temperature adjustment. Any changes in the setting or in the temperature disturb the balance of the kiln and require a long period for readjustment. Again, if the kiln is

running slowly enough to burn large shapes properly, it is running slower than necessary to burn standards bricks. Probably the most desirable condition would be to have one tunnel kiln running on 9-in. sizes and a second kiln on a slower schedule burning only large shapes.

A well-designed tunnel kiln will use from one-half to one-third of the fuel per thousand bricks required for a periodic kiln. In Table 53 are given some figures on the fuel consumption of tunnel kilns.

A tunnel kiln reduces the setting and handling cost in a unit by as much as 20 to 35 per cent, through the continuous flow of materials. In the case of dry-pressed bricks, it is general practice to set the tunnel-kiln cars directly from the dry press and then to pass them either through a drier or, in some cases, directly to the kiln. This eliminates drier cars, shods, and storage space for the drying bricks.

It is difficult to state definitely the relative qualities of a tunnel-kiln and a periodic-kiln product because the conditions are so varied. It may be said in general, however, that the tunnel-kiln product is more uniform than that of the periodic kiln, both as to size and as to degree of burning. This is due to a more even temperature in the small cross section of the tunnel kiln and to the fact that the stresses resulting from the height of the setting and the shrinking of the charge as a whole are much smaller in the tunnel kiln. Kiln marking is rarely found. The tunnel-kiln product is probably no better than the best of the periodic charge, but a large portion of the charge from the periodic kiln will undoubtedly be inferior to any of the tunnel-kiln product.

The cost of building a tunnel kiln to burn refractories will run about \$2,000 to \$3,500 per thousand bricks per day. This cost takes in only the kiln itself, and a complete unit for manufacturing 30,000 clay bricks per day would cost in the neighborhood of \$200,000 to \$250,000.

Undoubtedly, a modern tunnel-kiln unit can turn out bricks at a lower cost than the old periodic unit, because of both the saving of fuel and the saving of labor. This fact and the general belief that the product is superior to the periodic product have led many manufacturers to change over their plants to tunnel-kiln operation.

Tunnel kilns are used successfully to fire refractories other than fireclay. Silica bricks have been burned in tunnel kilns here and abroad for some time. A kiln for burning silica bricks at the rate of 35,000 bricks per day would be approximately 500 ft. long to give a comparatively long soak at the maximum temperature, which would run around 1500°C. (2732°F.). Magnesite and chrome bricks are being successfully burned in tunnel kilns. These bricks are not able to support a great load while they are being burned; and in periodic kilns, it was necessary to support them more or less completely with silica bricks. In a tunnel kiln, however, the setting can be made so low that the bricks are well supported during the burning operation, which gives a lower kiln loss and a superior product.

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CHAPTER XI

REFRACTORY MORTARS, PLASTICS, CONCRETES AND COATINGS

1. **Introduction.**—Refractory mortars are used in laying refractory brick and shapes and serve the following purposes: to bond the brickwork into a solid unit so that it will be more resistant to shocks and stresses, to provide a cushion between the slightly irregular surfaces of the brick so that one course of brickwork will have a firm bearing on the course below it, and also to make a wall gas tight or to prevent penetration of slag into the joints. The best mortars are combinations of a plastic clay and a volume-constant grog, as the use of raw fireclay alone as a mortar is confined to low-temperature applications.

Mortars are sometimes thinned with water and used as coatings for the face of the refractory walls in order to further seal the joints or to protect the wall from destructive elements in the furnace.

Plastic refractories are used for three general purposes. The first is for making molded refractory shapes to be used in the furnace in the green state; the second is to form a molded monolithic wall or furnace structure; and the third, to repair and patch worn brickwork.

Refractory concretes contain an aggregate and a setting material, such as hydraulic cement, to give them cold-setting properties. The aggregate may be calcined fireclay, which will give a high density to the concrete, or it may be a porous grog, diatomaceous earth, vermiculite, or other porous material to give light weight and low heat conductivity to the resulting concrete.

Hot patching materials are not used very extensively as yet but are intended for forming a stable refractory while the furnace is at operating temperatures.

The general composition of these refractory materials varies a great deal depending upon the application for which they are

intended. The majority are made from a fireclay base, but there are many special compositions in which chrome, silicon carbide, silica, and alumina are used. The manufacturer of the brick should be consulted when selecting a mortar or coating.

2. Fireclay Mortars. Heat-setting Types.—Mortars in this classification are generally composed of grog and a bond clay. No air-setting ingredient such as sodium silicate is added, and the mortar obtains its strength by the vitrification of the bond. For low-temperature service or where a strong mortar is needed, a clay high in fluxes should be used for the bond, whereas a mortar for high-temperature service would use a fireclay or kaolin. The nonplastic part is crushed to pass a 40-mesh screen and mixed with the bond. To reduce the shrinkage, the nonplastic ingredient may comprise as much as 60 per cent of the total mortar. Sufficient raw clay must be used, however, to give proper plasticity and workability, and therefore the clays must be carefully selected for this purpose. The size distribution of the nonplastic grog also affects the working properties of the mortar.

Heat-setting mortars are usually shipped in 100-lb. moisture-proof bags.

Air-setting Fireclay Mortars.—Air-setting mortars are composed of a base of precalcined fireclay or raw flint clay crushed to pass a 40-mesh screen. To this is added a plastic fireclay and from 5 to 20 per cent sodium silicate solution. The choice of plastic bond clay and the soda-silica ratio of the sodium silicate solution will determine the properties of the mortar. To obtain a mortar for severe temperature conditions, a highly refractory clay and a sodium silicate solution that has a low ratio of soda to silica should be chosen. For more moderate temperature service, a more plastic but less refractory clay combined with a sodium silicate solution richer in soda will give a mortar of better working properties and lower vitrifying point; but it will, of course, have a lower temperature use limit. The grog base should be sized so as to produce in the finished mortar the least drying and firing shrinkage compatible with good workability.

The water content of an air-setting mortar is adjusted until it has the consistency of a thick batter. On air drying, these mortars set to a good strength and form an almost monolithic structure with the brickwork, in some cases the mortar joint being stronger than the surrounding brick.

A batch mixing process is generally used to ensure good control of the tempering water added. After mixing, the mortar is packed in steel drums and sealed with rubber-gasketed steel lids. These containers are sold in 50-, 100-, and 200-lb. sizes.

For some special applications, a dry, air-setting mortar is desired. In this case, dry, powdered sodium silicate is used instead of the wet solution, the rest of the mortar remaining essentially the same. The air-set strength of these dry mortars, however, is not so great as that obtained with the wet mortars. Dry, air-setting mortar is packaged in moistureproof bags, usually in 100-lb. sizes.

Special Mortars.—For special applications, both heat-setting and air-setting mortars are made up using bases other than fireclay. Magnesite, chrome, silica, alumina, and silicon carbide are the more common ones and are used in laying up bricks of their respective materials. Alumina mortars are used where extreme temperature conditions are encountered and where freedom from iron is important. So-called “natural mortars” are much used in Europe. They consist of a naturally occurring clay and sand mixture with good working properties.

Application.—Mortar is generally applied in one of three ways, but it should be emphasized that in most cases, the thinnest possible joint is desired. The first method results in the so-called “battered joint,” where the mortar is mixed to a batter consistency and the top of the exposed course of brickwork is spread, using a trowel, with a thin coating. The brick to be laid is given a trowel coating on the bottom of one end and then tapped or pushed into place.

The second is known as the “dip” method. The mortar is thinned out with more water than when using battered joints. The brick to be laid is dipped into the thin batter on the bottom and on one end and then pushed into place. The thickness of the joint can be regulated by the consistency of the batter.

A combination method sometimes used consists of pouring a batter on to the exposed top course and then dipping the bricks to be laid on them. This results in more completely filled joints than the straight dipping method.

✓Approximately 400 lb. of mortar is required for setting 1,000 bricks.✓

✓*Tests for Refractory Mortars.*—A number of methods have been proposed for testing mortars. Phelps^(8a) describes some carefully

thought-out methods, which have been extended by Heindl and Pendergast.⁽¹⁴⁾

The fusion point can be determined by the methods described in Chap. XII; but when silicate of soda is present, a preliminary calcining of the material to 1100°C. is recommended by Phelps^(3a) in order to obtain consistent results. However, the fusion

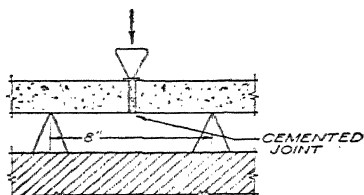


FIG. 181.—Method of measuring bonding strength.

point is not particularly valuable, and the block tests as used for glazes and enamels⁽¹⁴⁾ or the amount of flow of the mortar when used as a bond is more important.

The bonding range is generally determined by cementing two half bricks together on the $2\frac{1}{2}$ by $4\frac{1}{2}$ -in. faces with a definite thickness of joint. After drying, they are broken as shown in Fig. 181, or they may be heated to various temperatures and broken while heated or when cooled to room temperature. Care must be exercised to prevent any stresses in the samples due to movement of the pieces while drying; otherwise low values will result from fine cracks.

The shrinkage can be measured on bars of the mortar in the usual way or by the characteristics of a layer dried and fired on a brick. The coefficient of thermal expansion can be measured by the methods described in Chap. XVI.

The workability is an important property, but one difficult to measure. Troweling ability is measured by a machine developed by the U.S. Bureau of Standards,⁽¹⁴⁾ but it is generally better to depend on the reports of experienced bricklayers. Rate of settling is important in mortars used in the pouring consistency and is simple to evaluate. Water-retention values, as measured by Phelps,^(3a) are determined by cementing two half bricks together with no load and then, after a certain time interval, adding a load and noting the amount of mortar squeezed out. This test is particularly important for insulating refractories.

Resistance to erosion by slags or penetration by gases can be measured by methods described in Chaps. XV and XIX, respectively.

3. Plastics.—Plastic refractories are now being used in somewhat larger quantities than in the past; in some instances, quite large furnaces have been constructed of monolithic plastic material with good results. It should be noted that the plastic material fires hard only on the hot surface and has a weaker and more flexible zone on the cooler side. Although this may sometimes be a disadvantage, in other cases it actually seems to give a greater life than the burned refractory because of the flexibility of the wall. However, success can be obtained with plastics in large monolithic structures only by skilled application.

Fireclay Plastics.—Some of the plastic materials are cold setting; *i.e.*, they develop strength on drying. As in the case of cold-setting mortars, this strength is achieved by the addition of sodium silicate to the mass. Most of the plastics are made up with a base of fireclay grog, either specially prepared or made from waste brickbats and saggars. The maximum size of this grog runs from 4 to 2 mesh in order to reduce the drying and firing shrinkage. The bond clay used must be selected with great care to give good workability and low shrinkage.

It is particularly important that the plastics have a low drying and firing shrinkage; otherwise the structure will be badly cracked after the first firing. For this reason, the proportion of grog is comparatively large, running between 40 and 60 per cent of the total. Not only the maximum size of the grog is important in achieving good results, but the grading of the grog to give the best characteristics is quite important. The plastic mass should be of such consistency that it is coherent and sticks to the brickwork. It should not be crumbly when worked up or get soft and wet when hard rammed. A good plastic can be rammed into a patch in the crown without slumping or pulling away.

Ladle Mixes.—A considerable amount of plastic refractory called "ladle" or "ramming" mixes are used for lining ladles in the iron and steel industry and for pouring spouts and parts of that nature. These refractories must have rather special properties, such as good workability and a softening point approaching the pouring temperature of the metal, so that the surface of the refractory becomes glazed and offers good resistance to metal and slag attack. Whereas many of these mixes have bases of fireclay grog, others consist of a kaolin base and, in some cases, high-alumina clays have been used.

Special Plastics.—Besides the fireclay-base plastics, considerable quantities of chrome-base plastics are used, particularly under conditions of severe slag erosion. The important field for this class of plastics is in the stud walls of boiler furnaces where it can be rammed around the water-wall tubes to form a refractory capable of withstanding terrific punishment in the way of high temperatures and slag conditions. This type of plastic is usually made up of raw or calcined chrome ore with some clay bond and often silicate of soda. African or Cuban chrome ore is generally preferred for this use.

Silica ramming mixtures are made from crushed ganister or sandstone and fireclay as a bond. These mixes should be made up to have good workability and are used largely for patching cupolas and other metallurgical furnaces. Silicon carbide ramming mixtures are used where high heat transfer or good slag resistance are desired. Although comparatively expensive, they give excellent service under certain severe conditions. Magnesite ramming mixtures usually consist of dead-burned magnesite grain mixed with some organic bond like tar or dextrine. These are used for the basic electric furnaces, basic open-hearth furnaces, and some of the nonferrous constructions.

Application of Plastics.—Satisfactory service cannot be expected from plastic materials unless they are properly applied. The directions given by the maker of the plastic used should be carefully followed in order to ensure a first-class job. Although the methods vary somewhat depending on the type of plastic, in general the following steps should be taken in the application of this material.

In laying a plastic furnace bottom, such as plastic chrome ore in a forging furnace, it is customary to use the following procedure: Take the material out of the cans and dump it on a clean spot on the floor near the furnace, cutting the lumps with a spade but adding no water. If the material has to be left for any length of time, it should be covered with damp burlap bags to prevent its drying out. Beginning on one side of the furnace floor, lumps of the material should be spread out in a layer approximately 50 per cent thicker than the finished layer; *i.e.*, if a 3-in. floor is going to be put in, the thickness of the lump material should be 4 or 5 in. It is well to work in a strip about 30 in. wide beginning at one side of the furnace. * A heavy spade

then thoroughly cuts through the lumps with deep strokes so that the blanket of material is thoroughly tied together. Then, with a heavy tamper, the whole mass is consolidated with heavy strokes. The thickness of the layer should be tested with a rod. If it is too thin, the whole mass will have to be cut up again with a spade before adding more material; otherwise it will not consolidate. The final surface can be put on by laying boards on top and tamping on these. The next 30 in. strip can then be started, care being taken to ensure that it is well cut into the edge of the finished strip to make a bond. More boards can be laid on this, and the procedure repeated until the whole floor is done. The finished surface should not be walked on unless boards are put down.

It is good practice in all plastic construction to punch the layer with small vent holes about 2 in. deep to let out the steam on drying. This can be very conveniently done by making a rectangular frame into which spikes have been driven on about 3 in. centers. The frame can be readily pressed down on to the surface of the plastic.

In some cases, successful results have been obtained by tamping the hearth while it is hot with a heavy weight on the end of a pipe that can be introduced through the furnace door. If this tamping is carried out every week-end, the hearth soon becomes consolidated into an excellent structure.

When using plastic materials in side walls, wooden forms are required in order that the plastic can be rammed in to form a really monolithic structure. Sometimes plastic materials have been used for small furnace roofs where the ramming is done on top of a form. Generally, however, a refractory concrete would be used for this purpose.

Plastics are also used for patching walls; and under these conditions, great care must be taken to obtain a satisfactory piece of work. The wall itself must be carefully cleaned of any adhering slag, and the brickwork surface roughed up and, in some cases, undercut to hold the patch. This is usually hammered in with a heavy wooden mallet, precautions being used to build up the layer uniformly and without laminations. Figure 182 shows a patch of this kind which has been completed in a furnace.

Packing of Plastics.—Plastics are usually shipped wet in tightly sealed cans, although manufacturers sometimes pack a cube of

the mixture in waterproof paper and ship it in a carton. Occasionally, manufacturers have had trouble with air-setting plastics hardening in storage. A reason for this is suggested by Morgan, Peskin, and Kronman,⁽¹⁷⁾ who believe some clays adsorb soda from the sodium silicate and allow precipitation of silica gel. This subject needs more study.

Testing of Plastics.—The important characteristics of plastic materials are the fusion point, the workability, the reheat

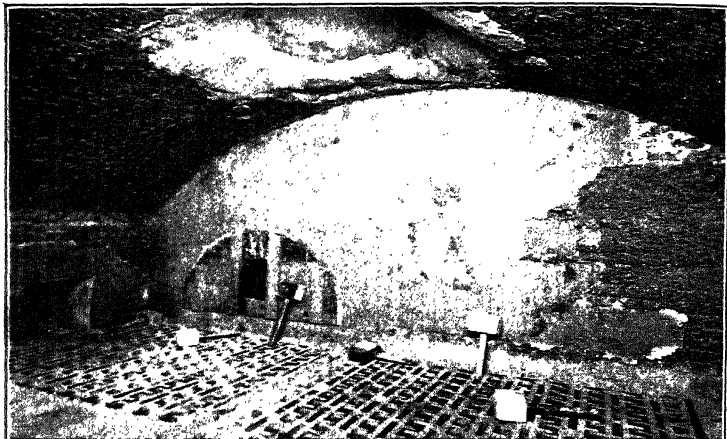


FIG. 182.—An example of furnace repairs with a plastic refractory. (Courtesy of A. P. Green Fire Brick Co.)

shrinkage as determined by the panel test, and the strength when fired to various temperatures. These tests have not been very well standardized, especially those concerning the workability, but many of the large users have their own specifications which they have found from experience will enable them to select a good material.

4. Refractory Concretes.—Refractory concretes are generally made up with a heavy grog to provide a dense, strong mass or with a porous grog to provide a light refractory. They are widely used for low- and medium-temperature work. Some important applications are the casting of baffles in boiler-tube banks, forming the lining of doors and the tops of tunnel-kiln cars, and, in some cases, the construction of special shapes.

Dense Mixes. These mixes are generally made up with 60 to 80 per cent fireclay grog, perhaps made from crushed brick bats, and 15 to 25 per cent early strength or high-alumina cement and clay for workability. The prepared mixes, of course, are always shipped dry, but often they are made up and mixed by the user, as he generally has available his own brickbats which can be readily crushed up for grog. It will be found, however, in general, that a carefully prepared batch made by a reliable manufacturer will give better results than mixes made up by the user. Refractory concretes can seldom be used above 2650°F. (about 1460°C.).

Lightweight Mixes.—These mixes are made up in a similar way to the previous one, except that the aggregate is of some lightweight material like lumps of infusorial earth, bloated clay, or porous grog. Lightweight mixes are used in such places as doors of furnaces and similar positions where the temperature is not extreme. Their density runs between 45 and 60 lb. per cu. ft.

All the refractory concretes have a low strength at a temperature of 1500 to 1800°F. (about 820 to 980°C.), where the cement is dehydrated and strength has not been attained by vitrification. This will give in the structure a weak layer that has not yet been overcome in this class of material. Nevertheless, these mixes are being used with considerable success in many types of structure.

Tests.—The tests of refractory concretes are similar to those mentioned for plastics, *i.e.*, the softening point, the drying and firing shrinkage, and the strength at various temperatures.

5. Refractory Coatings.—Refractory coatings are used to some extent on the surface of certain types of brickwork to close the pores and present a more homogeneous surface, thus minimizing abrasion and slag erosion. However, unwarranted claims have been made for coatings, claims that would indicate that a good coating would make a lower grade refractory give the service of a high-grade refractory. This is not generally true, and a coating is by no means a cure-all for refractory troubles.

Perhaps one of the best references on this subject is that by Litinsky,⁽²¹⁾ who discusses the subject thoroughly and gives a complete bibliography. A great many types of refractory coatings are available.

Natural Coatings.—Raw fireclay, which was used to some extent in the early days, has been more or less discarded because of its high shrinkage and tendency to peel off the brickwork. Natural coatings are used extensively in Europe containing clay, quartz, and feldspar in such proportions as to reduce the shrinkage and give a fluxing action. This material is very similar to the natural mortars previously discussed and generally has good working properties with a comparatively low cost.

Prepared Fireclay Coatings.—For high-temperature conditions, the coating used most frequently is a mixture of calcined grog with a plastic bond clay. A satisfactory coating should have a low shrinkage and adhere well to the brick so that no peeling or checking is observable on heating to the working temperature. The brick manufacturers' recommendation should be taken, because a coating that may work very well with one type of refractory may not work at all with another type, even though of very similar properties.

Special Coatings.—Many special coatings are available such as those with a chromite base or a chrome oxide base which are used to give some additional slag resistance to fireclay or insulating firebrick. There are also coatings having fused alumina or silicon carbide as a base for special purposes. They all must have the property, however, of low shrinkage and adherence to the brick with which they are used.

Application of the Coatings.—Coatings can be applied to the brickwork with a brush or with a spray gun. The latter is generally more satisfactory in giving a really good job. The coatings must be applied in comparatively thin layers, $\frac{1}{16}$ to $\frac{1}{8}$ in. being the maximum generally used. Even then, a better job is obtained by applying it in several successive applications if this is possible. About $\frac{1}{4}$ to $\frac{1}{2}$ lb. per sq. ft. of material should be allowed for an average coating job. Particular care should be taken that the brickwork is clean and free from dust before the coating is applied.

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PART III

Properties

CHAPTER XII

THE FUSION POINT OF REFRACTORY MATERIALS AND THEIR EQUILIBRIUM DIAGRAMS

1. **Fusion Process.**—At the present time, there is very little understanding of the mechanism concerning the fusing of non-metallic materials. If a curve of viscosity is plotted against temperature, it will be found that for some materials, the change from a solid to a liquid occurs within a very small temperature interval whereas in other materials, especially silicates, the melting process is a more gradual one and occurs over a large temperature range. As shown in Chap. IV, it will be found, in the case of materials having a long softening range, that there is a great difference in the bond strength between the various atoms. For example, in the silicates, the bond strength that holds the silicon in the center of an oxygen tetrahedron is very strong and probably will not break up until much higher temperatures are reached than are necessary to break the weaker bonds. Therefore, we may conceive that when a silicate fuses, at first the weaker bonds are broken and a very viscous liquid results which contains aggregates of the silicon-oxygen groups. As the temperature goes higher, these groups are broken up by thermal agitation until the viscosity markedly decreases. Unfortunately, we have no experimental evidence to show just what happens in this process and can merely conjecture a mechanism that most nearly fits the facts.

In the literature, it will be found that the terms "melting point," "softening point," and "fusion point" are used more or less indiscriminately in discussing refractories. The best usage would seem to indicate that the term melting point should be

reserved for pure materials and fusion or softening point for more complex or impure materials. It is, of course, difficult to draw a sharp boundary between the two; so it was thought best to use the term fusion point throughout this chapter for everything except the pure materials, as the majority of the refractories show a considerable softening range.

2. Method of Obtaining Fusion Points. *Physical Significance of the Fusion Point.*—There has been a great deal of confusion in considering just what is meant by the fusion point of the average refractory. We can do no better than refer to the method used by the glass technologist in determining the fusion or softening point of glass. Here, the fusion point is specified as the temperature at which the particular specimen under a definite stress becomes sufficiently fluid to flow at a specified rate. No other meaning will have any significance in discussing materials that have no sharp boundary between the solid and liquid state.

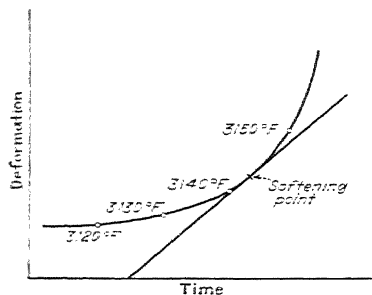


FIG. 183.—Method of determining the softening point.

This definition of fusion point can be made clear by the curve in Fig. 183 in which the deformation in millimeters of the specimen is plotted against the time, under the conditions where the specimen is heated up at a uniform rate. If we are arbitrarily assuming the fusion point as that temperature at which the rate of flow equals 0.01 mm. per sec., a tangent can be drawn to the flow curve with this slope. The point where the curve and tangent meet will represent the fusion temperature, which, in the illustration, is 3143°F. Owing to experimental difficulties, the usual methods of measuring the fusion points do not follow such an exact procedure; consequently, only an approximate value is obtained.

Determination of Fusion Points by Comparison with the Pyrometric Cones.—A common method of determining the fusion point is by comparing the bending characteristics of the sample with those of a series of standard pyrometric cones all run in the same

furnace. As it can be carried out by persons not skilled in pyrometric practice and with inexpensive equipment, this method has the advantage of simplicity. It has the disadvantage, however, of not giving the highest degree of precision, because of variations in the furnace atmosphere or from other causes that are not easy to control. Under good conditions, however, a precision of $\pm 15^{\circ}\text{C}$. (27°F .) should be obtained. The following quotation gives the standard A.S.T.M. softening-point test for refractory materials:

STANDARD METHOD OF TEST FOR PYROMETRIC CONE EQUIVALENT OF REFRACTORY MATERIALS

A.S.T.M. Designation C24-42¹

ADOPTED, 1920; REVISED, 1928, 1931, 1933, 1935, 1942

This Standard of the American Society for Testing Materials is issued under the fixed designation C24; the final number indicates the year of original adoption as standard or, in case of revision, the year of the last revision.

1. **Scope.**—This method is intended for determining the Pyrometric Cone Equivalent of fireclay, fireclay brick, silica cement, and ground fireclay by comparison of test cones with Standard Pyrometric Cones under the conditions herein prescribed.

2. **Preparation of Sample.** (*a*) *Clay or Brick.*—The entire sample of fireclay or fireclay brick, in case the amount is small, shall be reduced in size by means of rolls or a jaw crusher to a maximum size of $\frac{1}{4}$ in. In case the amount is large, a representative sample obtained by approved methods shall be so treated. The sample shall then be mixed thoroughly, and the amount reduced to about 250 g. (0.5 lb.) by quartering. Any magnetic material introduced by crushing or grinding shall be removed by means of a magnet. This portion shall then be ground in an agate, porcelain, or hard steel mortar, and the amount reduced again by quartering. The final size of the sample shall be 50 g., and the fineness such that it will pass a No. 70 ($210\ \mu$) A.S.T.M. sieve (equivalent to mesh No. 65 of the Tyler standard series). In order to avoid excessive reduction of fines, they shall be removed frequently during the process of reduction by throwing the sample on the sieve and continuing the grinding of the coarser particles until all the sample will pass through the sieve.

(*b*) *Silica Cements.*—In the case of silica cements, the sample obtained by approved methods shall be tested as received without grinding or other treatment.

¹ A.S.T.M. Standards are subject to revision. The Society's headquarters, in Philadelphia may be consulted for the latest information.

NOTE: For the purpose of this test, silica cement is understood to be the usual finely ground mixture of quartzite, silica brick, and fireclay of various proportions, and does not include materials sold under the name of high-temperature mortars.

3. Preparation of Test Cones.—*a.* The dried sample shall be thoroughly mixed and, after the addition of sufficient dextrine, glue, gum tragacanth, or other alkali-free organic binder and water, shall be formed in a truncated trigonal pyramid with its base at a small angle to the trigonal axis; and of the following dimensions: Over-all height (between planes perpendicular to the trigonal axis) 1½ in.; length of the side of the trigonal tip, 0.075 in.; length of the two longer sides of the base, ¾ in.; base at an external angle of 82 deg. to one face and perpendicular to the symmetry plane through the opposite edge of the pyramid.

b. When dry, the test cones may be subjected, when necessary, to a preliminary burn at a temperature not exceeding 2370°F. (1300°C.) for the purpose of sintering them into a firm condition to permit handling.

4. Mounting.—The test cones shall be mounted on plaques of refractory material of such a composition as will not affect the fusibility of the cones.* They shall be mounted with the base embedded approximately

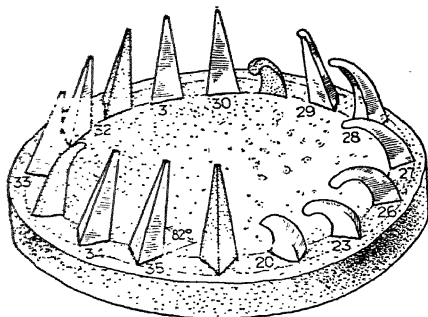


FIG. 183a.—Method of mounting test cones and appearance after testing.

3 mm. (0.12 in.) in the plaque, and the face of one side inclined at an angle of 82 deg. with the horizontal. The arrangement of the test cones with respect to the Standard Pyrometric Cones shall be substantially as shown in Fig. 183a, *i.e.*, alternating the test cones with the Standard Pyrometric Cones in so far as practical (Note, p. 387). The plaque

* A mixture of equal parts of a highly refractory clay such as a good grade of china clay and fused alumina which will pass a No. 100 (149 μ) A.S.T.M. sieve (equivalent to mesh No. 100 of the Tyler standard series) has been found satisfactory.

may be any convenient size and shape and may be biscuited before using, if desired.

NOTE: The number of cones and their mounting so as to face inward as shown in Fig. 183*a* is typical for gas-fired furnaces of relatively large dimensions and gases moving at high velocity. The practical bore of the muffle tubes in most electric furnaces does not permit cone pats of this size. The static atmosphere prevailing permits the cones being mounted to face outward, if so desired.

5. Heating.—*a.* The heating shall be carried out in a suitable furnace at a rate to conform to the following requirements:

	Minutes		Minutes
To reach cone No. 20.....	45	Time interval to:	
Time interval to:		Cone 32.....	8
Cone No. 23.....	20	Cone No. 32½.....	9
Cone No. 26.....	6	Cone No. 33.....	9
Cone No. 27.....	4	Cone No. 34.....	6
Cone No. 28.....	4	Cone No. 35.....	10
Cone No. 29.....	10	Cone No. 36.....	10
Cone No. 30.....	4	Cone No. 37.....	4
Cone No. 31.....	12	Cone No. 38.....	6

NOTE: At 1830°F. (1000°C.) the old cone pat may be removed and a new one put in without cooling the furnace down below red heat.

b. That type of furnace in which a neutral or oxidizing atmosphere may be maintained is to be preferred. Excessive reducing conditions should be avoided. Care should be taken that the flame does not strike directly against the cone or cone plaque. The furnace should be tested at intervals for the determination of the uniformity of the distribution of the heat.

6. Pyrometric Cone Equivalent.—*a.* The softening of the cone will be indicated by the top bending over and the tips touching the plaque. The bloating, squatting or unequal fusion of small constituent particles should always be reported. The Pyrometric Cone Equipment shall be reported in terms of Standard Pyrometric Cones and shall be that cone which most nearly corresponds in time of softening with the test cone. If the test cone softens later than one Standard Pyrometric Cone but earlier than the next Standard Pyrometric Cone and approximately midway between, the P.C.E. shall be reported thus: Cone No. 31-32.

b. If the test cone starts bending at an early cone but is not down until a later cone, the fact should be reported.

Determination of Fusion Points with the Optical Pyrometer.—

A more precise determination of the fusion point can be made with the optical pyrometer, which is sighted on the test specimen heated in a furnace under black-body conditions. With ordinary care, a precision of $\pm 7^{\circ}\text{C}$. (about 12.6°F .) should be obtained;

and with especial care in calibration, a precision of $\pm 4^{\circ}\text{C}$. (about 7.2°F .) is possible.

Most of the fusion points have been made on specimens formed into a slender tetrahedron similar in shape to the standard pyrometric cone. This particular form of specimen has commonly been used because the bending can readily be seen without special measuring apparatus, but it does have certain disadvantages for precise work: because (1) the size of the specimen varies, depending on the shrinkage of the refractory material; (2) the density of the specimen varies with the material so that the bending forces are variable; and (3) the bending forces vary with the position of the cone.

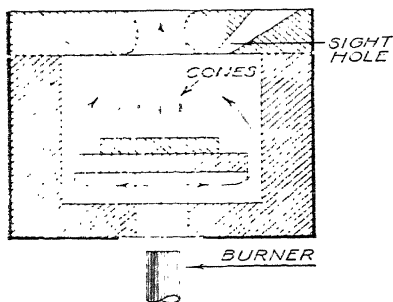


FIG. 184.—A gas-fired fusion-point furnace.

Apparently a much better form of specimen for fusion-point tests would be a small bar supported at its ends. On heating, this bar will soften and sag in the middle. By sighting on the center of the bar with a reading telescope, it is possible to plot the amount of settling against time and thus obtain a curve capable of giving a precise value of fusion point as shown in Fig. 183. Certain precautions are necessary, however, in this type of test: (1) The material should be precalcined in order to shrink it to a stable volume, and (2) the distance between the supports should be so arranged as to give a definite stress in the specimen based on its density and cross-sectional area.

Furnaces for Determining Fusion Points.—Fusion points can be determined in a cylindrical type of furnace heated by a gas and air burner up to temperatures of 1700°C . (about 3090°F .). Figure 184 shows such a furnace for determining fusion points

in comparison with pyrometric cones. For higher temperatures, the same type of furnace can be used with oxygen instead of air, in which case temperatures as high as 2000°C . (about 3630°F .) can be reached. Von Wartenberg⁽⁴³⁾ obtained temperatures up to 2600°C . (about 4710°F .) with oil and oxygen, and Hauser⁽⁵¹⁾ has used the oxyhydrogen flame for very high-temperature fusions. The main difficulties in this type of furnace are the shielding of the specimens from the high-velocity gases, the producing of real black-body conditions, and the maintaining of an oxidizing or neutral atmosphere.

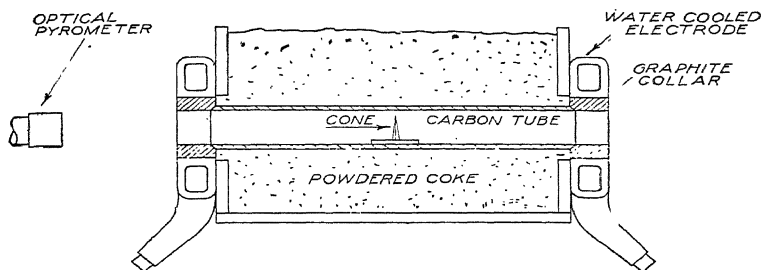


FIG. 185.—A horizontal electric tube furnace.

One of the most convenient methods of determining fusion point is in the electric tube furnace. A very convenient type is the horizontal furnace shown in Fig. 185, which was developed a number of years ago in the Heat Measurements Laboratory at the Massachusetts Institute of Technology. Any temperature up to 2400°C . (about 4350°F .) can be quickly obtained under good black-body conditions. A gas flame placed at either end of the tube prevents the entrance of oxygen and thus preserves the carbon tube. This furnace will, of course, produce a strong reducing atmosphere, which is often undesirable in making fusion points. It is quite simple, however, to put inside the carbon tube a refractory liner through which a small flow of air is drawn, thus giving a strictly oxidizing atmosphere for fusion-point work. Such refractory tubes may be made of magnesite, magnesia spinel, or zirconia, but great care must be taken to prevent reaction between the fusion-point specimen and the tube. The vertical-tube furnace of Pendergast⁽¹³⁾ can be used up to 1825°C . (about 3320°F .) with an oxidizing atmosphere.

REFRACTORIES

The high-frequency induction furnace as shown in Fig. 186 is quite suitable for high-temperature research, but here again the heating element is a graphite crucible or sleeve, and to obtain oxidizing atmospheres it is necessary to use a liner through which air can be drawn.

Wire-wound furnaces have been used for high temperatures. Platinum furnaces can be used up to temperatures of 1500°C. (about 2730°F.), which is hardly high enough for fusion-point

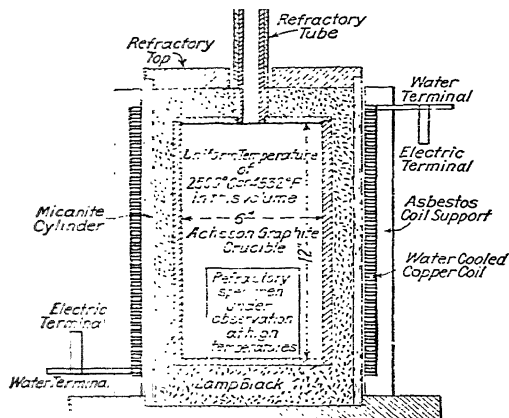


FIG. 186.—A high-frequency induction furnace. (*J. Ind. Eng. Chem.*)

work. However, windings of molybdenum or tungsten are quite satisfactory up to 1700 and 2000°C. (about 3090 and 3630°F.), respectively, if a hydrogen atmosphere is used to protect the windings. However, there is the disadvantage of the strong reducing atmosphere that greatly influences the fusion point of materials containing iron.

The vacuum furnace shown in Fig. 187 has been used a great deal for the determination of fusion points of very refractory materials. The melting is carried out in a vacuum, although in the furnace there must be traces of carbon monoxide gas which tends to produce reducing conditions. The heat is supplied by a graphite spiral resistance which surrounds the specimen. The metal case, which is evacuated, is placed in a water bath to keep the temperature down. It is possible, with

this furnace, to reach temperatures of 3000°C . (about 5430°F .); but since the chamber has to be evacuated before each test, it is not so convenient to operate as some of the other types mentioned.

Preparation of Fusion-point Specimens.—In making up specimens for fusion-point determinations, it is very essential that representative samples be taken. For example, if the

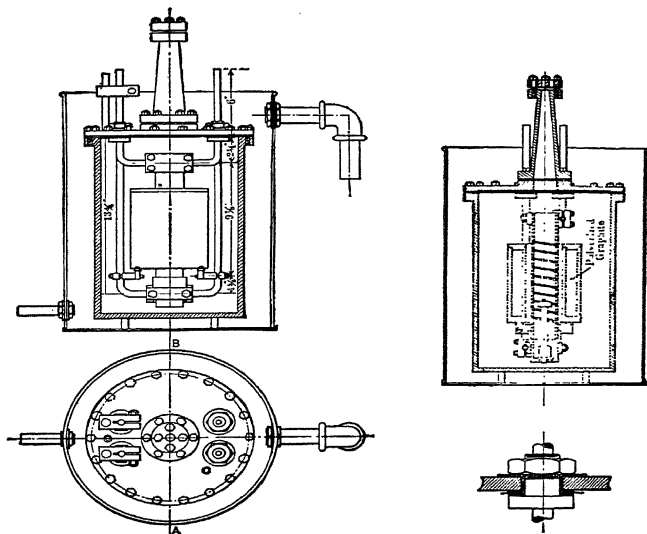


FIG. 187.—An Arsem vacuum furnace. (*J. Am. Ceram. Soc.*)

fusion point of a brick is desired, the brick should be broken up and a number of random samples taken. These fragments are then ground so that they will completely pass a 65-mesh screen. Grinding should be carried out at first in a steel mortar; and if the material is very hard, iron specks should be removed with a magnet. The final grinding should be done in an agate mortar. In the case of clay the usual sampling methods should be employed in order to ensure representative results. In the case of lump clay, such as bauxite, it will be found that the hard nodules have a higher melting point than soft material; therefore

a considerable amount must be crushed and split down to a small sample. A riffle sampler such as that shown in Fig. 188 is excellent for the purpose.

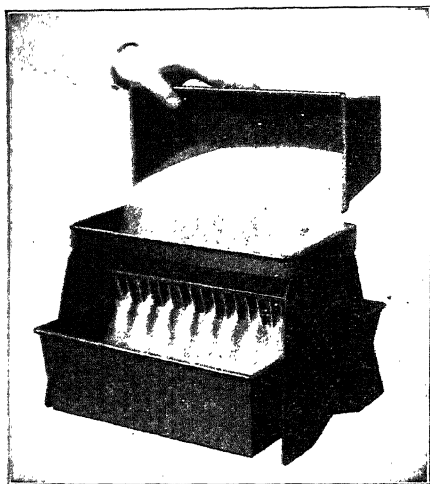


FIG. 188.—A riffle sampler. (Courtesy of W. S. Tyler Company.)

The sample is moistened with water and pressed with a spatula into a mold. With nonplastic materials, an organic binder is used. It is usually desirable to make the cones small, as they will more readily follow the temperature of the furnace. A cone 1 in. high with a $\frac{3}{16}$ in. triangular base, according to the standard of the American Society for Testing Materials, is very satisfactory. A mold for making these cones is shown in Fig. 189. Considerable manipulative skill is required to make and handle cones made from lean or sandy materials.

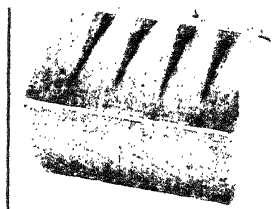


FIG. 189.—A mold for making test cones.

The cones should be carefully dried before being placed in the melting furnace; and if they are fragile, they should be given sufficient preliminary heating to frit them together. In placing

a cone on a boat, it is a good idea to cut a shallow recess and cement the base of the cone into it; but great care should be taken to make this cement out of the identical material from which the cone is made, as otherwise a reaction may occur that will give a fusion point considerably too low. In every case, the cone should be placed so that the face will make an angle of 82 deg. with the horizontal, as shown in Figs. 190 and 191.

Effect of Atmosphere on Fusion Point.—The fusion point of pure silica or alumina is little, if at all, influenced by the furnace

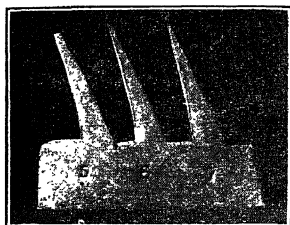


FIG. 190.—Cones ready for placing in the kiln. (Courtesy of The Standard Pyrometric Cone Company.)

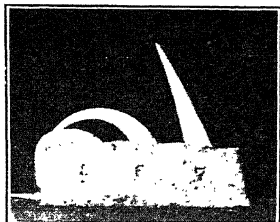


FIG. 191.—Cones after firing. Cone 6 is just down. (Courtesy of The Standard Pyrometric Cone Company.)

atmosphere; however, when any impurity is present, especially iron oxide, the atmosphere does have a marked effect on the fusion point. Just why the reduced oxide should combine more readily with the other constituents to form a low-melting compound is not known. Fieldner, Hall, and Feild⁽²⁾ found that when the iron oxide in the mixture was reduced to the metallic condition below the softening temperature, little lowering of the fusion point resulted. Apparently the act of reduction makes the iron oxide more active in combining with the other constituents.

The influence of the atmosphere on the fusion point of fireclay containing very finely divided iron oxide is shown by the results of Vickers and Theobald.⁽⁶³⁾ The effect of the reducing gases is very marked (Fig. 192) and shows that the lowering of the fusion point increases almost directly with the iron oxide content.

Test cones in a reducing atmosphere seldom bend over smoothly. Often a hard coating forms, allowing the molten center to run out at the base. Fusion points should be taken

only when the test cone bends down gradually until the tip touches the base, as in *A* of Fig. 193. When a cone bends only at the base, as in *B*, it is probable that interaction has occurred

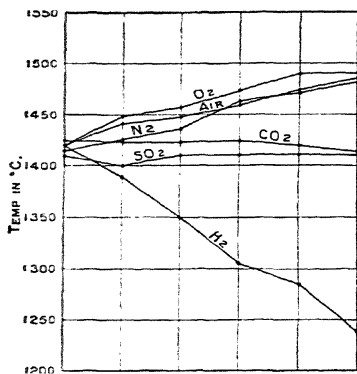


FIG. 192.—Curves showing the fusion temperatures of a clay containing various proportions of finely divided ferric oxide in various gases.

between the cone and the plaque. Some materials even under the best conditions will not give good readings but will either bloat, *C*, or slump down, *D*. Unless for some special purpose, fusion points should always be made in an oxidizing or neutral atmosphere.

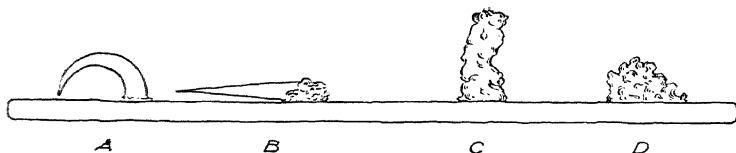


FIG. 193.—Behavior of specimen cones on firing.

3. Fusion Point and Composition.—A number of relations have been suggested to connect the chemical composition of a clay with its fusion point. Perhaps the earliest work on this subject was that of Richter, who showed that various fluxes had equal effects if they were taken in molecular equivalents; *i.e.*, 40 parts of MgO would have the same influence on a clay as 94 parts of K_2O . He also stated that if a number of fluxes are

present, their influence is proportional to the sum of their equivalents. We know now that these relations are not strictly true, but this work was a great step forward in logical procedure.

Richter's law has been applied to fireclay by Ludwig,⁽¹⁴⁾ who found the law restricted to certain conditions, such as low concentrations and intimate mixtures.

Schuen⁽²⁰⁾ gives for the fusion point of a clay, in degrees centigrade, the following formula:

$$\frac{360 + \text{Al}_2\text{O}_3 - \text{RO}}{0.228}$$

The Al_2O_3 and RO are given in percentage weight, so calculated that the Al_2O_3 and SiO_2 equal 100. He finds that although this formula gives fair average results, there are many other important influences, such as grain size and state of oxidation.

H. Salmang⁽¹⁸⁾ and Hohler^(21a) have studied the influence of grain size on the fusion point. They find that the finer the grain the lower the fusion value.

Chiywskii⁽¹⁵⁾ and Tschischewslay⁽²¹⁾ have tried to correlate the amount of the water of constitution with the fusion point.

Many attempts have been made to correlate the atomic structure of a crystal with its melting point, for it should be possible to determine this value from the bond strengths in the molecule. Although certain correlations exist in some of the simple structures like a series of alkali halides, the structures are, in general, too complicated to handle directly. However, it is possible to formulate a few general rules from the data available, based on the discussion of this subject in Chap. IV.

In the first place, the only compounds having high fusion points are borides, carbides, nitrides, and oxides. It is interesting to notice that the four elements boron, carbon, nitrogen, and oxygen are adjacent to one another in the periodic table. They all have two electrons in the inner, or K, shell and three, four, five, and six electrons, respectively, in the outer shell. Although we do not have particularly accurate values of fusion point for the high-temperature materials, it would seem reasonable to expect that the small number of electrons in the outer shell of this series correspond to the higher fusion point. Such a correlation is listed in Table 54. There are little data on the melting point of the fluorides, and none listed goes above 1400°C . (about

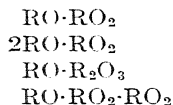
2550°F.). It should be remembered that most of the nitrides, carbides, and borides are unstable in an oxidizing atmosphere.

TABLE 54.—CORRELATION OF MELTING POINT AND ATOMIC STRUCTURE

Element	Oxide, °C.	Nitride, °C.	Carbide, °C.	Boride, °C.
Ti	1850	2930	3140	
Ca	2570		2300	
Si	1710		>2700 d	
Ta	1470 d	3090	3880	
W	1473		2877	2920
V	1970	2050	2830	
Zr	2720	2980	2750	2990
Hf	2812	3310	3530	3065
U	2176		2400	

It will also be noticed that all the high-melting point compounds have a valence number of 2 or over, and a general tendency indicates that the higher the ionic bonding the higher the fusion point. We may also note that all the refractory materials have a high hardness, generally over 6, if we neglect the unstable materials containing the CO_2 or OH groups. Then again, the refractory materials generally have a high density, very few being below 3.0. Although very little data are available, there is evidence to indicate that materials having the lowest volume compressibility are the most refractory, which would also follow from our conception of high bond strength.

In considering the more complicated compounds of a refractory nature, it is interesting to note that practically all of them fall into the following four groups:



4. Melting Point of Some Refractory Materials.—Table 55 shows the melting points of pure refractory materials in so far as they are at present available. It should be realized that the determination of the fusion points of these very refractory materials presents great difficulties and that undoubtedly more refined work will alter many of them in the future.

TABLE 55.—MELTING POINTS OF PURE REFRACTORY MATERIALS
Elements

Material	Formula	Melting point		Sp. Gr.
		°C.	°F.	
Graphite.....	C	3500	6300	2.5
Tungsten.....	W	3370	6100	19.0
Tantalum.....	Ta	2850	5160	16.6
Osmium.....	Os	2700	4890	22.5
Molybdenum.....	Mo	2650	4800	9.0
Ruthenium.....	Ru	2450	4440	12.1
Iridium.....	Ir	2350	4260	22.4
Boron.....	B	2300	4170	2.5
Rhodium.....	Rh	1955	3550	12.4
Columbium.....	Cb	1950	3540	8.4
Uranium.....	U	1850+	3360	18.7
Thorium.....	Th	1845	3350	11.5
Titanium.....	Ti	1800	3270	4.5
Platinum.....	Pt	1775	3240	21.4
Vanadium.....	V	1710	3110	5.7
Zirconium.....	Zr	1700	3090	6.4

TABLE 55.—MELTING POINTS OF PURE REFRACTORY MATERIALS.—
(Continued)
Oxides

Material	Mineral or common name	Formula	Melting point		Sp. Gr.
Aluminum oxide.....	Alumina	Al ₂ O ₃	2050 ⁽³⁷⁾	3722	4.0 ⁽³⁷⁾
Barium oxide.....		BaO	1923 ⁽³⁷⁾	3493	5.72 ⁽⁵⁷⁾
Beryllium oxide.....	Bromellite	BeO	2510 ⁽⁵⁸⁾	4550	3.0 ⁽³⁷⁾
Calcium oxide.....	Lime	CaO	2570 ⁽³⁷⁾	4658	3.4 ⁽³⁷⁾
Cerium oxide.....	Ceria	CeO ₂	2810 ⁽³⁷⁾	5090	7.3 ⁽⁵⁷⁾
Chromium oxide.....		Cr ₂ O ₃	2275 ⁽³⁰⁾	4127	5.27 ⁽⁵⁷⁾
Cobalt oxide.....		CoO	1800 ⁽⁵⁸⁾	3272	6.47 ⁽⁶¹⁾
Columbium oxide.....		Cb ₂ O ₅	1520 ⁽³⁷⁾	2768	4.60 ⁽⁵⁷⁾
Gallium oxide.....		Ga ₂ O ₃	1740 ⁽⁵⁸⁾	3164	α 6 44.65, SS ⁽⁶¹⁾
Hafnium oxide.....	Hafnia	HfO ₂	2812 ⁽⁵⁹⁾	5094	9.68 ⁽⁶¹⁾
Iron oxide.....	Hematite	Fe ₂ O ₃	1560d ⁽⁵⁷⁾	2840d	5.1 ⁽³⁷⁾
Iron oxide.....	Magnetite	Fe ₃ O ₄	1538d ⁽⁵⁷⁾	2800d	5.2 ⁽⁵⁷⁾
Lanthium oxide.....	Lanthia	La ₂ O ₃	2320 ⁽⁵⁸⁾	420S	6.51 ⁽⁵⁷⁾
Lithium oxide.....	Lithia	Li ₂ O	>1700 ⁽⁵⁷⁾	>3092	2.01 ⁽⁵⁷⁾
Magnesium oxide.....	Periclase	MgO	2800 ⁽⁵⁷⁾	5072	3.5 ⁽⁵⁷⁾
Manganese oxide.....	Manganosite	MnO	1650 ⁽⁵⁷⁾	3002	5.1S ⁽⁵⁷⁾
Nickel oxide.....	Bunsenite	NiO	1960 ⁽⁵⁸⁾	3560	7.45 ⁽⁶¹⁾
Silicon oxide.....	Cristobalite	SiO ₂	1710 ⁽⁵⁷⁾	3110	2.32 ⁽⁵⁷⁾
Strontium oxide.....	Strontia	SrO	2430 ⁽⁵⁸⁾	4406	4.7 ⁽⁵⁷⁾
Tantalum oxide.....		Ta ₂ O ₅	1470d ⁽⁵⁷⁾	2678d	8.73 ⁽⁵⁷⁾
Thorium oxide.....	Thoria	ThO ₂	3030 ⁽⁵⁴⁾	5486	9.69 ⁽⁵⁷⁾

TABLE 55.—MELTING POINTS OF PURE REFRACTORY MATERIALS.—
(Continued)
Oxides (Cont.)

Material	Mineral or common name	Formula	Melting point		Sp. Gr.
			°C.	°F.	
Titanium oxide	Titania	TiO ₂	1850 ⁽⁵⁰⁾	3362	4.2 ⁽⁵⁷⁾
Tungsten oxide		WO ₃	1473 ⁽⁵⁷⁾	2683	7.16 ⁽⁶¹⁾
Uranium oxide		UO ₂	2176 ⁽⁵⁷⁾	3949	5.6 ⁽⁵⁷⁾
Vanadium oxide		VO	2050 ⁽⁶¹⁾	3722	
Vanadium oxide		VO ₂	1967 ⁽⁶¹⁾	3573	4.40 ⁽⁵⁷⁾
Vanadium oxide		V ₂ O ₅	1970 ⁽⁵⁷⁾	3578	4.87 ⁽⁵⁷⁾
Yttrium oxide	Yttria	Y ₂ O ₃	2410 ⁽⁵⁷⁾	4370	4.84 ⁽⁵⁷⁾
Zinc oxide	Zincite	ZnO	>1800 ⁽⁵⁷⁾	>3272	5.60 ⁽⁵⁷⁾
Zirconium oxide	Zirconia	ZrO ₂	2720 ⁽³²⁾	4928	5.6 ⁽⁵⁷⁾

Silicates

Aluminum silicate	Mullite	3Al ₂ O ₃ ·2SiO ₂	1810 ^{d(57)}	3290 ^d	3.0 ⁽⁵⁷⁾
Barium silicate	Metasilicate	BaO·SiO ₂	1605 ⁽⁵⁷⁾	2921	4.4 ⁽⁵⁷⁾
Barium silicate		BaO·2SiO ₂	1420 ⁽⁴¹⁾	2588	3.73 ⁽⁵⁷⁾
Barium silicate	Orthosilicate	2BaO·SiO ₂	>1755 ⁽⁵⁷⁾	>3191	3.84 ⁽⁵⁷⁾
Barium silicate		2BaO·3SiO ₂	1450 ⁽⁴¹⁾	2642	3.93 ⁽⁵⁷⁾
Barium aluminum silicate	Celsian	BaO·Al ₂ O ₃ ·2SiO ₂	>1700 ⁽⁵⁷⁾	>3092	3.37 ⁽⁵⁷⁾
Barium calcium silicate		BaO·2CaO·3SiO ₂	1320 ^{d(38)}	2408	
Barium zirconium silicate		BaO·ZrO ₂ ·SiO ₂	1573 ^(61a)	2864	4.65 ⁽⁵⁷⁾
Beryllium silicate	Metasilicate	BeO·SiO ₂	>1755 ⁽⁵⁷⁾	>3191	
Beryllium silicate	Orthosilicate	2BeO·SiO ₂	2000 ⁽⁵⁷⁾	3632	3.0 ⁽⁵⁷⁾
Beryllium aluminum silicate	Beryl	3BeO·Al ₂ O ₃ ·6SiO ₂	1410 ⁽⁵⁷⁾	2570	2.66 ⁽⁵⁷⁾
Calcium silicate		3CaO·SiO ₂	1900 ⁽⁵⁷⁾	3452	
Calcium silicate	Orthosilicate	2CaO·SiO ₂	2130 ⁽⁵⁷⁾	3866	3.3 ⁽⁵⁷⁾
Calcium silicate		3CaO·2SiO ₂	1475 ⁽³⁷⁾	2687	
Calcium silicate	Pseudowollastonite	CaO·SiO ₂	1540 ⁽⁵⁷⁾	2804	2.91 ⁽⁶¹⁾
Calcium aluminum silicate	Anorthite	CaO·Al ₂ O ₃ ·SiO ₂	1550 ⁽⁵⁷⁾	2822	2.77 ⁽⁶¹⁾
Calcium aluminum silicate	Gehlenite	2CaO·Al ₂ O ₃ ·SiO ₂	1590 ⁽⁵⁷⁾	2894	3.04 ⁽⁵⁷⁾
Calcium magnesium silicate	Monticellite	CaO·MgO·SiO ₂	1498 ^{d(37)}	2728	3.2 ⁽⁵⁷⁾
Calcium potassium silicate		CaO·K ₂ O·SiO ₂	1620 ⁽⁴⁶⁾	2948	
Calcium zirconium silicate		CaO·ZrO ₂ ·SiO ₂	1582 ^(61a)	2880	4.3
Iron silicate	Grunerite	FeO·SiO ₂	1550 ⁽⁵⁷⁾	2822	3.5 ⁽⁵⁷⁾
Magnesium silicate	Ferroite	2MgO·SiO ₂	1890 ⁽⁵⁷⁾	3434	3.2 ⁽⁵⁷⁾
Magnesium silicate	Clino-enstatite	MgO·SiO ₂	1557 ^{d(57)}	2835 ^d	3.28 ⁽⁵⁷⁾
Magnesium zirconium silicate		MgO·ZrO ₂ ·SiO ₂	1793 ^(61a)	3260	4.35 ⁽⁵⁷⁾
Manganese silicate	Tephroite	2MnO·SiO ₂	1320 ^{d(41)}	2408 ^d	4.04 ⁽⁵⁷⁾
Potassium aluminum silicate	Kaliophilite	K ₂ O·Al ₂ O ₃ ·2SiO ₂	1790 ⁽³⁰⁾	3254	2.6 ⁽⁵⁷⁾
Potassium aluminum silicate	Leucite	K ₂ O·Al ₂ O ₃ ·4SiO ₂	1810 ⁽³⁴⁾	3290	2.47 ⁽⁵⁷⁾
Silica	Cristobalite	SiO ₂	1710 ⁽⁵⁷⁾	3110	2.32 ⁽⁵⁷⁾
Sodium zirconium silicate		Na ₂ O·ZrO ₂ ·SiO ₂	1708 ^(61a)	3107	3.58 ^(61a)
Sodium aluminum silicate	Nephelite	Na ₂ O·Al ₂ O ₃ ·2SiO ₂	1526 ⁽⁵⁷⁾	2779	2.60
Strontium silicate		2SrO·SiO ₂	>1700 ⁽⁵⁷⁾	>3092	3.84 ⁽⁵⁷⁾
Strontium silicate		SrO·SiO ₂	1580 ⁽⁵⁷⁾	2876	3.65 ⁽⁵⁷⁾

TABLE 55.—MELTING POINTS OF PURE REFRACTORY MATERIALS.—
(Continued)
Silicates (Cont.)

Material	Mineral or common name	Formula	Melting point		Sp. Gr.
			°C.	°F.	
Strontium aluminum silicate.....	Willemite	$\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$> 1700^{(57)}$	> 3092	
Zinc silicate.....		$2\text{ZnO} \cdot \text{SiO}_2$	$1509^{(57)}$	2748	3.9 ⁽⁵⁷⁾
Zinc zirconium silicate...	Zircon	$\text{ZnO} \cdot \text{ZrO}_2 \cdot \text{SiO}_2$	$2078^{(61a)}$	3773	4.57 ^(61a)
Zirconium silicate.....		$\text{ZrO}_2 \cdot \text{SiO}_2$	$2500^{(57)}$	4532	4.5 ⁽⁵⁷⁾

Aluminates (Other than Spinels)

Calcium aluminate.....		$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	$1455^{(29)}$	2651	
Calcium aluminate.....		$3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$	$1720^{(29)}$	3128	
Calcium aluminate.....		$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$1535^{d(29)}$	2795	
Calcium ferric aluminate..		$4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	$1415^{(44)}$	2579	
Calcium sodium aluminate.		$3\text{CaO} \cdot 2\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$	$> 1630^{(48)}$	> 2966	
Calcium sodium aluminate.		$8\text{CaO} \cdot \text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3$	$1503^{d(48)}$	2746 ^d	
Lithium aluminate.....		$\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$	$> 1625^{(57)}$	> 2957	2.55 ⁽⁵⁷⁾
Sodium aluminate.....		$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$	$1650^{(57)}$	3002	
Titanium aluminate.....		$\text{TiO}_2 \cdot \text{Al}_2\text{O}_3$	$1860^{(53a)}$	3380	

Nitrides

Aluminum nitride.....		AlN	$2150^{(57)}$	3902	3.05 ⁽⁶¹⁾
Beryllium nitride.....		Be_3N_2	$2200^{(57)}$	3992	
Hafnium nitride.....		HfN	$3310^{(59)}$	5990	
Tantalum nitride.....		TaN	$3090^{(59)}$	5594	
Titanium nitride.....		TiN	$2330^{(57)}$	5306	5.18 ⁽⁵⁷⁾
Vanadium nitride.....		VN	$2050^{(57)}$	3722	5.63 ⁽⁵⁷⁾
Zirconium nitride.....		ZrN	$2980^{(58)}$	5396	

Titanates

Beryllium titanate.....		$3\text{BeO} \cdot \text{TiO}_2$	$1810^{(46)}$	3290	
Beryllium titanate.....		$\text{BeO} \cdot \text{TiO}_2$	$1720^{(56)}$	3128	
Calcium titanate.....		$\text{CaO} \cdot \text{TiO}_2$	$1980^{(54)}$	3596	
Calcium titanate.....		$2\text{CaO} \cdot \text{TiO}_2$	$1800^{(54)}$	3272	
Calcium titanate.....		$3\text{CaO} \cdot \text{TiO}_2$	$1840^{(54)}$	3344	
Magnesium titanate.....		$2\text{MgO} \cdot \text{TiO}_2$	$1830^{(51)}$	3326	
Magnesium titanate.....		$\text{MgO} \cdot 2\text{TiO}_2$	$1670^{(51)}$	3038	
Manganese titanate.....	Pyrophanite	$\text{MnO} \cdot \text{TiO}_2$	$1404^{(57)}$	2559	4.54 ⁽⁵⁷⁾

Borides

Hafnium boride.....		HfB	$3065^{(59)}$	5549	
Iron boride.....		Fe_2B_5	$1340^{(57)}$	2444	
Iron boride.....		Fe_3B_2	$1351^{(57)}$	2464	
Tungsten boride.....		WB ₆	$2920^{(58)}$	5288	
Zirconium boride.....		ZrB ₃	$2990^{(58)}$	5414	

TABLE 55.—MELTING POINTS OF PURE REFRACTORY MATERIALS.—
(Continued)
Carbides

Material	Mineral or common name	Formula	Melting point		Sp. Gr.
			°C.	°F.	
Boron carbide		B ₄ C	2350 ⁽⁶¹⁾	4262	2.5 ⁽⁶¹⁾
Calcium carbide		CaC ₂	2300 ⁽⁵⁷⁾	4172	2.22 ⁽⁵⁷⁾
Chromium carbide		Cr ₃ C ₂	1890 ⁽⁵⁷⁾	3434	6.7 ⁽⁵⁷⁾
Chromium carbide		Cr ₇ C ₃	1665 ⁽⁵⁷⁾	3020	6.9 ⁽⁵⁷⁾
Graphite		C	>3600 ⁽⁶⁵⁾	>5432	2.25 ⁽⁵⁷⁾
Hafnium carbide		HfC	3330 ⁽⁵⁰⁾	6386	
Iron carbide		Fe ₃ C	1837 ⁽⁵⁷⁾	3339	7.4 ⁽⁵⁷⁾
Molybdenum carbide		MoC	2570 ⁽⁵⁷⁾	4658	8.4 ⁽⁵⁷⁾
Molybdenum carbide		Mo ₆ C	2380 ⁽⁵⁷⁾	4316	8.9 ⁽⁵⁷⁾
Silicon carbide		SiC	>2700 ⁽⁵⁷⁾	>4892 ^d	3.17 ⁽⁵⁷⁾
Tantalum carbide		TaC	3880 ⁽⁵⁵⁾	7016	
Titanium carbide		TiC	3140 ⁽⁵⁵⁾	5684	4.25 ⁽⁶¹⁾
Tungsten carbide		WC	2777 ⁽⁵⁷⁾	5031	15.7 ⁽⁵⁷⁾
Tungsten carbide		W ₂ C	2877 ⁽⁵⁷⁾	5211	16.06 ⁽⁵⁷⁾
Tungsten carbide		W ₃ C	>2700 ⁽⁵⁷⁾	>4892	
Uranium carbide		UC ₂	2260 ⁽⁵⁷⁾	4100	11.3 ⁽⁵⁷⁾
Uranium carbide		UC ₃	2400 ⁽⁵⁷⁾	4352	11.3 ⁽⁵⁷⁾
Vanadium carbide		V ₄ C ₃	2750 ⁽⁵⁷⁾	4982	
Vanadium carbide		VC	2830 ⁽⁵⁷⁾	5126	5.4 ⁽⁵⁷⁾
Zirconium carbide		ZrC ₂	2750 ⁽⁵⁷⁾	4982	
Zirconates					
Barium zirconate		BaO·ZrO ₂	2620 ⁽⁵⁷⁾	4748	
Calcium zirconate		CaO·ZrO ₂	2350 ⁽⁵⁵⁾	4262	4.78 ⁽⁶¹⁾
Magnesium zirconate		MgO·ZrO ₂	2150 ⁽⁵¹⁾	3902	
Strontium zirconate		SrO·ZrO ₂	>2800 ⁽⁵⁷⁾	>5073	
Phosphates					
Aluminum phosphate		AlPO ₄	>1500 ⁽⁵⁷⁾	>2732	2.56 ⁽⁵⁷⁾
Calcium phosphate		Ca ₃ (PO ₄) ₂	1670 ⁽⁵⁷⁾	3038	3.14 ⁽⁵⁷⁾
Calcium phosphat		Ca ₂ P ₂ O ₇	1630 ⁽⁵⁷⁾	2966	3.06 ⁽⁵⁷⁾
Calcium phosphat		10CaO·3P ₂ O ₅	1540 ⁽⁵⁷⁾	2804	2.89 ⁽⁵⁷⁾
Calcium phosphate of sand	Fluorapatite	CaF ₂ ·3Ca ₂ P ₂ O ₇	1630 ⁽⁵⁷⁾	2966	3.18 ⁽⁵⁷⁾
Sodium silico phosphate		5CaO·SiO ₂ ·P ₂ O ₅	1760 ⁽⁵⁷⁾	3200	3.01 ⁽⁵⁷⁾
Spinel					
Barium aluminate		BaO·Al ₂ O ₃	2000 ⁽⁶¹⁾	3632	
Calcium aluminate		CaO·Al ₂ O ₃	1600 ⁽⁵⁷⁾	2912	3.67 ⁽⁶¹⁾
Corund aluminate		CoO·Al ₂ O ₃	1960 ⁽⁶¹⁾	3560	
Pyroalus aluminate	Hercynite	FeO·Al ₂ O ₃	1600 ⁽⁵⁰⁾	2912	4.22 ⁽⁵³⁾
Pyroalus chromate	Chromite	FeO·Cr ₂ O ₃	>1770	>3218	4.93 ⁽⁵⁰⁾
Pyroalus ferrite	Magnetite	FeO·Fe ₂ O ₃	1538 ^(2/61)	2800	5.18 ⁽⁵³⁾
Magnesium aluminate	Spinel	MgO·Al ₂ O ₃	2135 ⁽⁵⁷⁾	3875	3.53 ⁽⁵³⁾
Magnesium chromite		MgO·Cr ₂ O ₃	>1750 ⁽⁵¹⁾	>3236	4.41 ⁽⁵³⁾
Magnesium ferrite	Magnesi-ferrite	MgO·Fe ₂ O ₃	>1780 ⁽⁵¹⁾	>3236	4.61 ⁽⁵³⁾
Nickel aluminate		NiO·Al ₂ O ₃	2020 ⁽⁵⁰⁾	3668	
Strontium aluminate		SrO·Al ₂ O ₃	2020 ⁽⁵¹⁾	3668	
Zinc aluminate	Gahnite	ZnO·Al ₂ O ₃	1950 ⁽⁵²⁾	3542	4.54 ⁽⁵³⁾
Zinc ferrite		ZnO·Fe ₂ O ₃	1590 ⁽⁶¹⁾	2894	5.27 ⁽⁵³⁾

In Table 56, the fusion points of a number of refractory bricks are given. These values were obtained with an optical pyrometer in a tube furnace under reducing conditions and, in many cases, will be slightly lower in value than a corresponding determination made in an oxidizing atmosphere.

TABLE 56.—FUSION POINTS OF BRICKS MANUFACTURED FROM NATIVE CLAYS

Material	Fusion point °C.	
Alumina, Fused.....	1750 to 2050	3182 to 3722
Bauxite.....	1732 to 1850	3150 to 3362
Carborundum (recrystallized).	2200 (decom.)	3992
Carbon.....	very high	
Chrome.....	1950 to 2200	3542 to 3992
Clay, native in:		
Arkansas.....	1615 to 1625	2939 to 2954
British Columbia.....	1615 to 1645	2939 to 2993
California.....	1657 to 1688	3015 to 3070
Colorado.....	1585 to 1796	2885 to 3265
England.....	1620 to 1637	2948 to 3015
Georgia.....	1685 to 1700	3065 to 3092
Idaho.....	1660 to 1700	3038 to 3092
Kentucky.....	1627 to 1718	2961 to 3124
Maryland.....	1595 to 1640	2903 to 2984
Missouri.....	1610 to 1750	2930 to 3182
Montana.....	1580	2876
New Jersey.....	1582 to 1677	2880 to 3051
New York.....	1685	3065
Ohio.....	1610 to 1782	2930 to 3240
Pennsylvania.....	1630 to 1757	2966 to 3195
Texas.....	1615	2939
Washington.....	1605 to 1638	2921 to 2980
Clays high in alumina.....	1802 to 1880	3276 to 3416
Graphite-clay.....	1605 to 1675	2921 to 3047
Kaolins (southern).....	1645 to 1785	2993 to 3245
Magnesite.....	2200	3992
Mullite.....	1780 to 1800	3236 to 3272
Silica.....	1700	3090
Spinel.....	1693 to 2100	3079 to 3812
Zircon and Zirconia.....	2200 to 2700	3992 to 4892

5. Value of Fusion Points.—The value of a fusion point in determining the possibility of a material for specific purposes has

often been overestimated. What the fusion point does show is whether or not a material is unsuitable above a certain temperature. For example, if it should be desired to make a firebrick to be used with furnace temperatures of 1600°C. (about 2910°F.), and various samples of clays were selected, the fusion-point test would eliminate at once all those with a fusion point equal to or below that temperature. However, a clay softening at 1850°C. (about 3360°F.) would not necessarily be better for this brick than another clay softening at 1750°C. (about 3180°F.).

The fusion point of a material is by no means a criterion of its ability to carry a load at high temperatures, which in actual use is of considerable importance in determining the maximum temperature at which it can be successfully used. For example, commercial magnesite has a fusion point of over 2000°C. (about 3630°F.); yet it will not carry a load at temperatures over 1400°C. (about 2550°F.) to 1500°C. (about 2730°F.). On the other hand, a mullite brick that has a fusion point of 1780°C. (about 3230°F.) will show no deformation at temperatures of 1727°C. (about 3140°F.).

6. Equilibrium Diagrams.—The equilibrium diagrams in the refractory systems are particularly useful in studying problems in the manufacture and use of refractories. A thorough understanding of the equilibrium conditions will allow one to interpret the results of practical tests more accurately, although it should be remembered that ceramic reactions seldom reach complete equilibrium. In this chapter are included nearly all of the equilibrium diagrams that are now available dealing with the refractory systems.

Phase Rule.—The construction and interpretation of the equilibrium diagram depends largely on the phase rule, which states

$$P + V = C + 2$$

where P = the number of phases

C = the number of components

V = the number of degrees of freedom

The following definitions applying to the equilibrium system are commonly used:

1. *System:* Any portion of the material universe that we choose to separate in thought from the rest of the universe for the purpose of considering and discussing the various changes that may occur within it under various conditions is called a "system."

2. *Phase*: The physically homogeneous but mechanically separable portions of the system are called its "phases."

3. *Components*: The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase may be quantitatively expressed.

4. *Variance of a System (Degree of Freedom)*: In the application of the phase rule to the type of systems under consideration, the independently variable conditions usually taken into consideration are temperature, pressure, and concentration. The number of these variables, which must be arbitrarily fixed to define the system completely, is called the "variance" or "degree of freedom" of that system.

5. *Equilibrium*: An equilibrium exists in any system under a fixed set of conditions when the parts of the system do not undergo any change of properties with the passage of time and provided the parts of the system have the same properties when the same conditions are again arrived at by a different procedure.

6. *Melting Point*: The temperature of transition of solid to liquid state at atmospheric pressure in which the liquid phase is of the same composition as the solid phase is known as the "congruent melting point" of the solid phase. This is in contradistinction to the transition of one solid phase into a second solid phase with the liberation of liquid of a different composition; the latter is called an "incongruent melting point."

7. *Transition Point*: When the pressure is the atmospheric pressure, the temperature at which two solid phases can coexist and at which the relative stability of the two forms undergoes change is known as the "transition point."

Methods of Obtaining High-temperature Equilibrium Diagrams. Although the method of using cooling curves has been of great aid to the metallurgist, it has not been successful for high-temperature refractory materials because of the great undercooling encountered and the small heat evolved or absorbed compared with radiation exchange. Heating curves are somewhat more reliable but not generally useful for studies of refractories.

The method most used consists in heating the mixture at a given temperature until equilibrium is established and quenching suddenly to fix the structure developed. A microscopic examination will then show the crystalline phases present, if any.

Interpretation of the Equilibrium Diagram.—For a full discussion of the interpretation of the equilibrium diagrams, reference should be made to Hall and Insley.^(61b) However, a very brief outline is given here to indicate the features of the simpler types of diagrams.

Let us first consider a phase diagram composed of two materials completely soluble in each other and forming no compound.

As an example, we may take lime and magnesia, shown in the diagram in Fig. 194. It will be noted that the solution of either

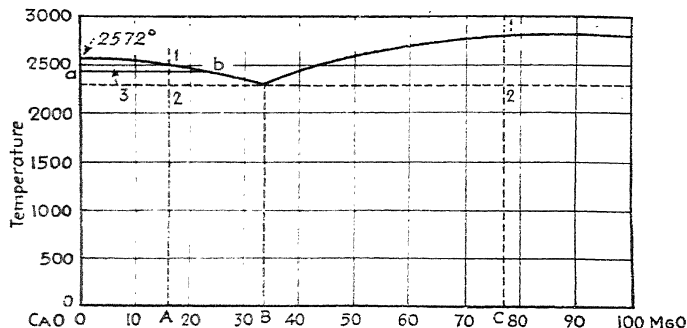


FIG. 194.—Equilibrium diagram for lime and magnesia. (Weight per cent.)

material in the other lowers the freezing point and that at a composition of 33 per cent MgO, the lowest freezing point is reached. When a composition represented by A is considered,

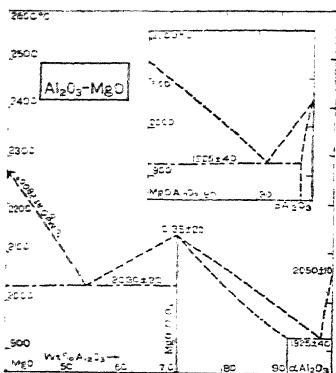


FIG. 195.—Equilibrium diagram for magnesia and alumina. *International Critical Tables.*

the melt is completely liquid above the point 1; but at this point, CaO begins to crystallize out. At the point 2, no liquid is left and the solid consists of mixed crystals of MgO and CaO. The same thing occurs at composition C, except that MgO first crystallizes out. At the composition B, CaO and MgO crystallize out simultaneously and there is no mixture of liquid and crystals as there are for all other compositions. This point is called the "eutectic point."

Another example may be considered where two substances are completely soluble in each other but form a single compound, such as magnesia and alumina. The simplified equilibrium diagram for these materials is shown in Fig. 195. The compound

TABLE 57.—EQUILIBRIUM DIAGRAMS

Binary Aluminates	
BaO·Al ₂ O ₃ (Fig. 203)	CoO·ZrO ₂ (Fig. 209)
BeO·Al ₂ O ₃ (Figs. 204, 205)	Fe ₂ O ₃ ·ZrO ₂ (Fig. 209)
CaO·Al ₂ O ₃ (Figs. 196, 203, 206, 208)	MgO·ZrO ₂ (Figs. 210, 223, 225)
CeO ₂ ·Al ₂ O ₃ (Figs. 204, 207)	Mn ₂ O ₄ ·ZrO ₂ (Fig. 209)
CoO·Al ₂ O ₃ (Fig. 203)	NiO·ZrO ₂ (Fig. 209)
Cr ₂ O ₃ ·Al ₂ O ₃ (Figs. 197, 204)	SrO·ZrO ₂ (Fig. 224)
Cu ₂ O·Al ₂ O ₃ (Fig. 204)	ZnO·ZrO ₂ (Fig. 209)
FeO·Al ₂ O ₃ (Fig. 198)	Beryllium Oxide Systems
Fe ₃ O ₄ ·Al ₂ O ₃ (Fig. 204)	CaO·BeO (Figs. 205, 220, 226)
Ga ₂ O ₃ ·Al ₂ O ₃ (Fig. 204)	CeO ₂ ·BeO (Figs. 205, 207)
La ₂ O ₃ ·Al ₂ O ₃ (Fig. 204)	CoO·BeO (Fig. 205)
MgO·Al ₂ O ₃ (Figs. 199, 203, 210)	Cu ₂ O·BeO (Fig. 205)
Mn ₂ O ₄ ·Al ₂ O ₃ (Fig. 204)	Fe ₃ O ₄ ·BeO (Fig. 205)
NiO·Al ₂ O ₃ (Fig. 203)	La ₂ O ₃ ·BeO (Fig. 205)
SiO ₂ ·Al ₂ O ₃ (Figs. 200, 203)	MgO·BeO (Figs. 205, 228)
SrO·Al ₂ O ₃ (Fig. 203)	Mn ₂ O ₄ ·BeO (Fig. 205)
ThO ₂ ·Al ₂ O ₃ (Fig. 204)	NiO·BeO (Fig. 205)
TiO ₂ ·Al ₂ O ₃ (Figs. 201, 203)	TiO ₂ ·BeO (Fig. 227)
ZnO·Al ₂ O ₃ (Fig. 202)	Calcium Oxide Systems
ZrO ₂ ·Al ₂ O ₃ (Figs. 204, 209)	CeO ₂ ·CaO (Fig. 207)
Binary Chromates	CoO·CaO (Fig. 220)
BeO·Cr ₂ O ₃ (Fig. 205)	Cu ₂ O·CaO (Figs. 208, 220)
CaO·Cr ₂ O ₃ (Fig. 206)	Fe ₂ O ₃ ·CaO (Figs. 206, 229)
CeO ₂ ·Cr ₂ O ₃ (Fig. 207)	MgO·CaO (Figs. 220, 228, 230)
MgO·Cr ₂ O ₃ (Fig. 210)	Mn ₂ O ₄ ·CaO (Figs. 220, 226)
ZrO ₂ ·Cr ₂ O ₃ (Fig. 209)	NiO·CaO (Fig. 220)
Binary Silicates	Ceric Oxide Systems
BaO·SiO ₂ (Fig. 211)	Fe ₃ O ₄ ·CeO ₂ (Fig. 207)
CaO·SiO ₂ (Figs. 206, 212)	MgO·CeO ₂ (Figs. 207, 228)
FeO·SiO ₂ (Fig. 213)	Mn ₂ O ₄ ·CeO ₂ (Fig. 207)
MgO·SiO ₂ (Figs. 210, 214)	Magnesium Oxide Systems
MnO·SiO ₂ (Fig. 215)	BaO·MgO (Fig. 228)
SrO·SiO ₂ (Fig. 216)	CoO·MgO (Fig. 210)
TiO ₂ ·SiO ₂ (Fig. 217)	Cu ₂ O·MgO (Fig. 228)
ZnO·SiO ₂ (Fig. 218)	Fe ₃ O ₄ ·MgO (Fig. 210)
ZrO ₂ ·SiO ₂ (Fig. 219)	Mn ₂ O ₄ ·MgO (Fig. 210)
Binary Thorates	NiO·MgO (Fig. 210)
BeO·ThO ₂ (Fig. 205)	SrO·MgO (Fig. 228)
CaO·ThO ₂ (Fig. 220)	Ternary Aluminates
TiO ₂ ·ThO ₂ (Fig. 221)	CaO·MgO·Al ₂ O ₃ (Fig. 231)
Binary Titanates	CaO·SiO ₂ ·Al ₂ O ₃ (Fig. 232)
CaO·TiO ₂ (Figs. 206, 208)	MgO·SiO ₂ ·Al ₂ O ₃ (Fig. 233)
MgO·TiO ₂ (Fig. 210)	ZnO·SiO ₂ ·Al ₂ O ₃ (Fig. 234)
Binary Zirconates	Ternary Silicates
BaO·ZrO ₂ (Fig. 224)	CaO·MgO·SiO ₂ (Fig. 235)
BeO·ZrO ₂ (Figs. 205, 225)	CaO·FeO·SiO ₂ (Figs. 236, 237)
CaO·ZrO ₂ (Figs. 206, 222, 224, 226)	MgO·FeO·SiO ₂ (Fig. 238)
CeO ₂ ·ZrO ₂ (Fig. 207, 209)	Ternary Zirconates
(CeO ₂ ·Ce ₂ O ₃)·ZrO ₂ (Fig. 209)	BeO·CaO·ZrO ₂ (Fig. 239)
	BeO·CeO ₂ ·ZrO ₂ (Fig. 240)
	CaO·ThO ₂ ·ZrO ₂ (Fig. 241)
	MgO·ThO ₂ ·ZrO ₂ (Fig. 242)

spinel is formed of a composition containing 72 per cent MgO and 28 per cent Al_2O_3 . The diagram may be divided into two portions, each one of which is similar to the preceding diagram.

It is possible to determine the relative amount of liquid and solid at any point of the diagram by the so-called "lever principle." Figure 194 gives the ratio of solid material at point 3 to liquid by

$$\frac{\text{Distance } b3}{\text{Distance } a3}$$

measuring along the horizontal line ab .

Equilibrium Diagrams for High-temperature Systems.—In Table 57 are listed nearly all the diagrams of interest in the refractories field, together with the figure numbers of the corresponding diagrams that follow. These diagrams were taken from Hall and Insley, published in the *Journal of the American Ceramic Society* (161b).

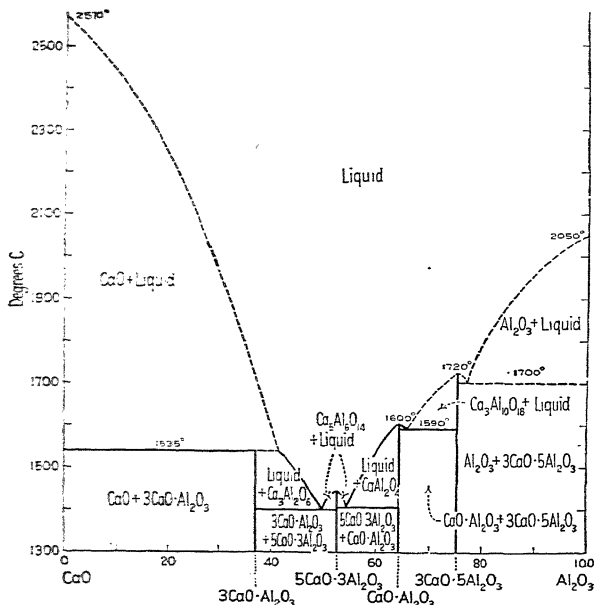


FIG. 196.—(Mol per cent.)

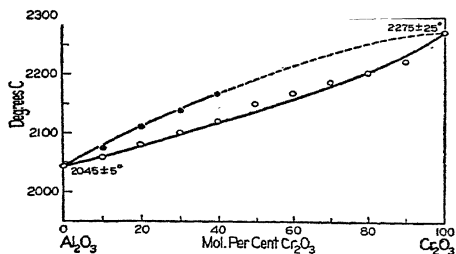


FIG. 197.

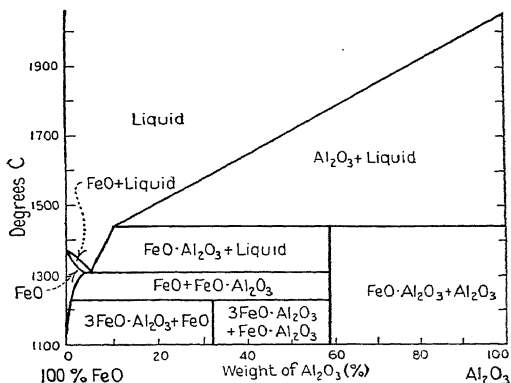


FIG. 198.

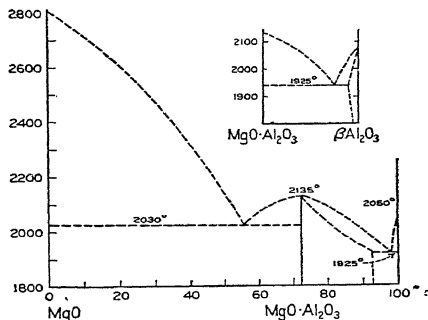


FIG. 199.—(Weight per cent.)

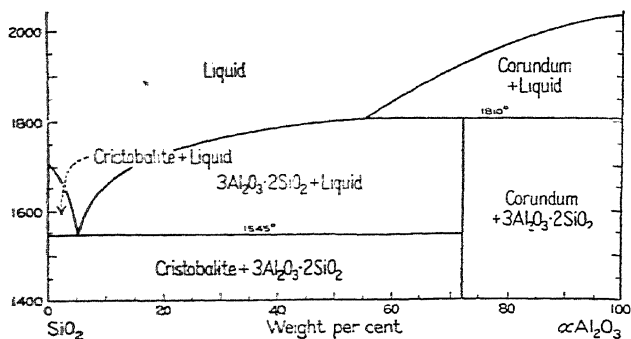


FIG. 200.

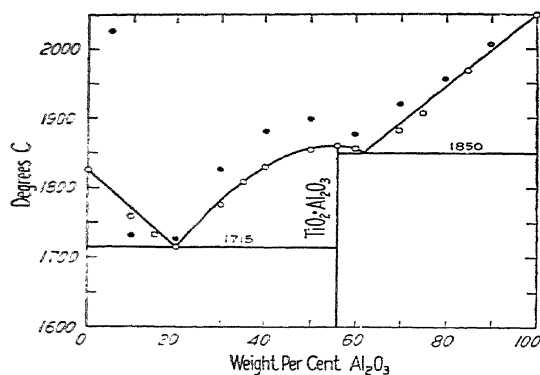


FIG. 201.

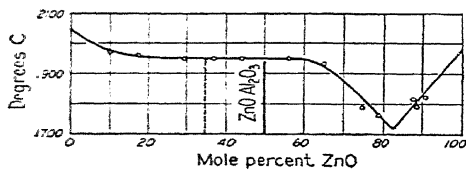


FIG. 202.

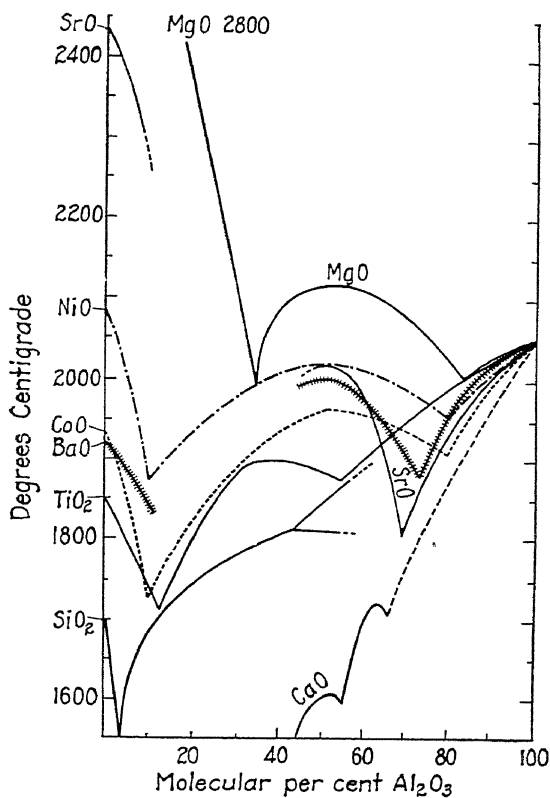


FIG. 203.

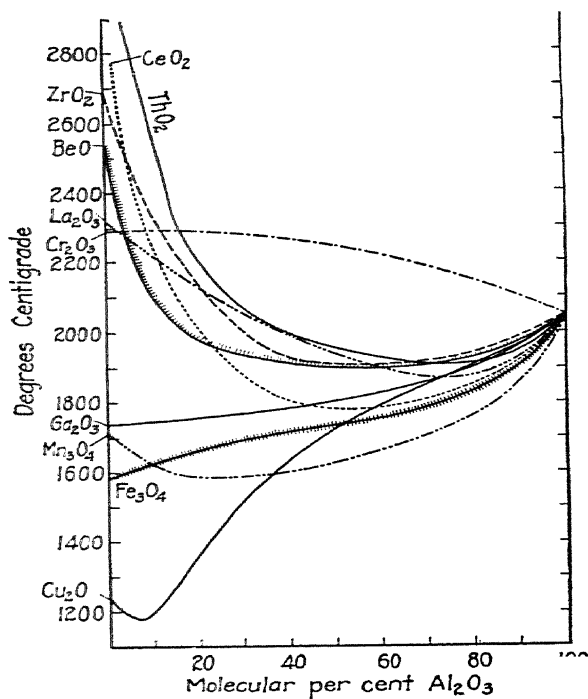


FIG. 204.

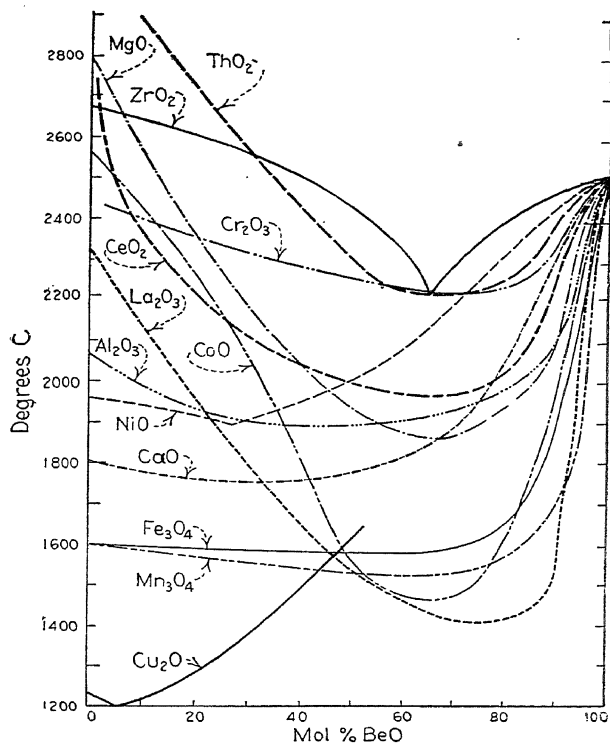


FIG. 205.

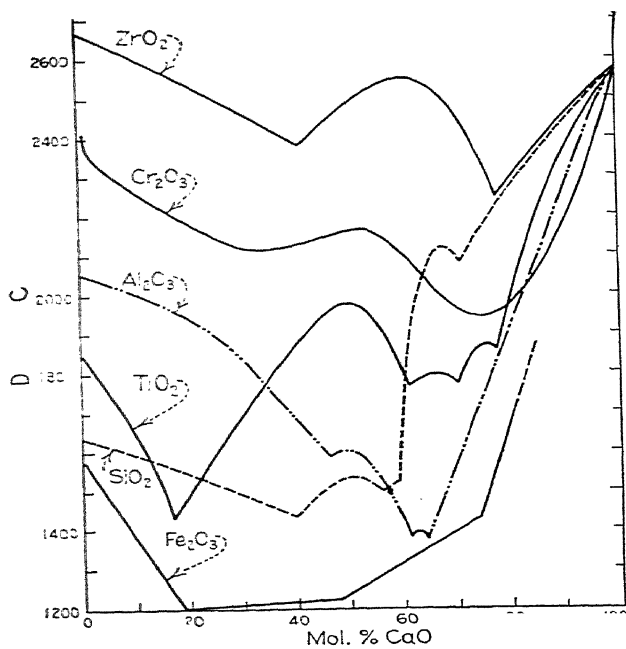


FIG. 206.

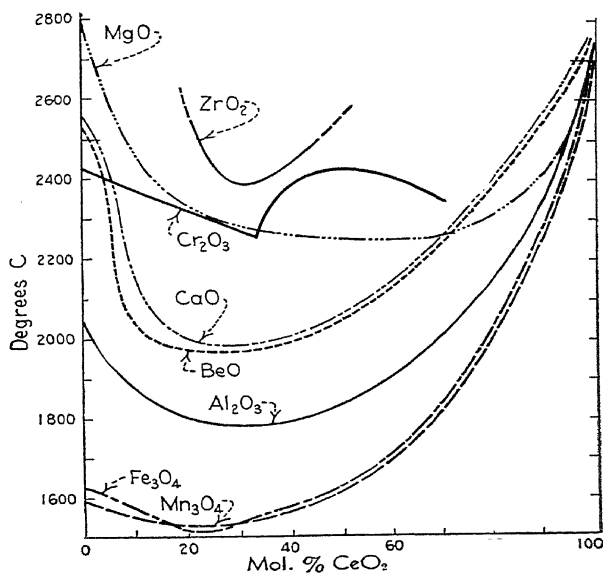


FIG. 207.

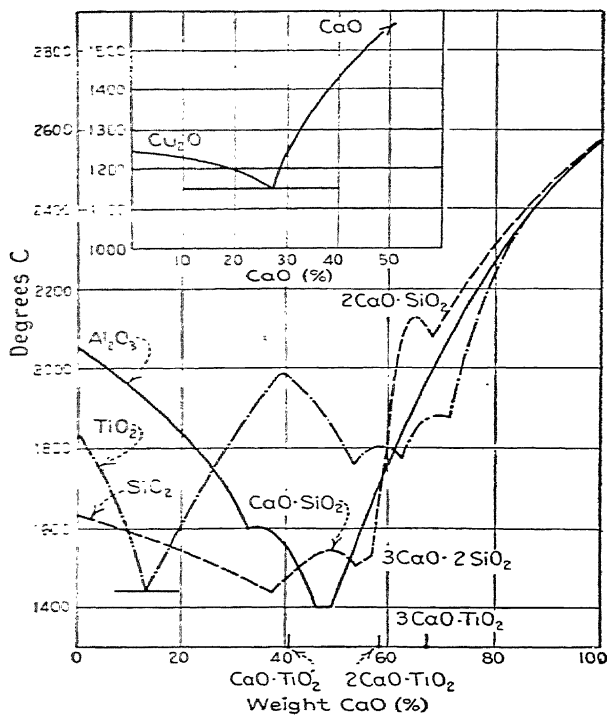


FIG. 208.

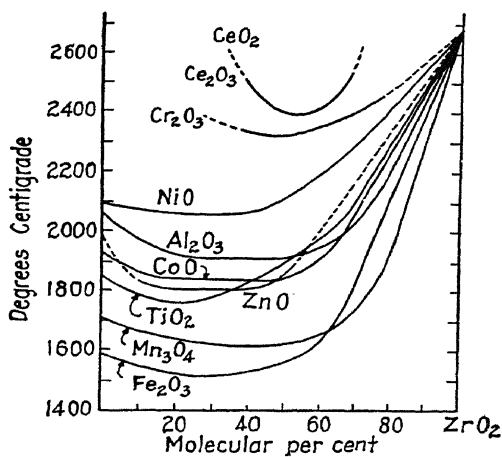


FIG. 209.

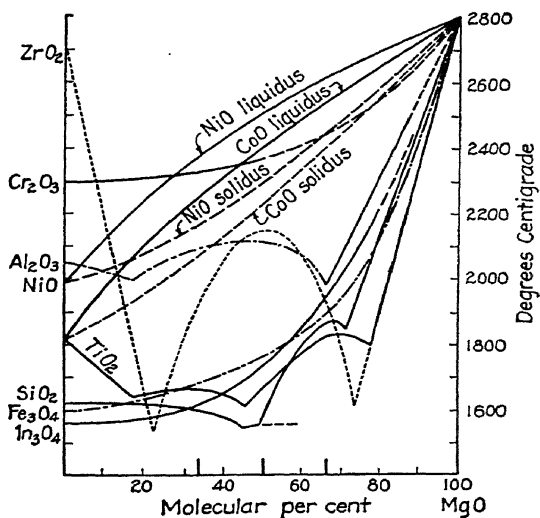


FIG. 210.

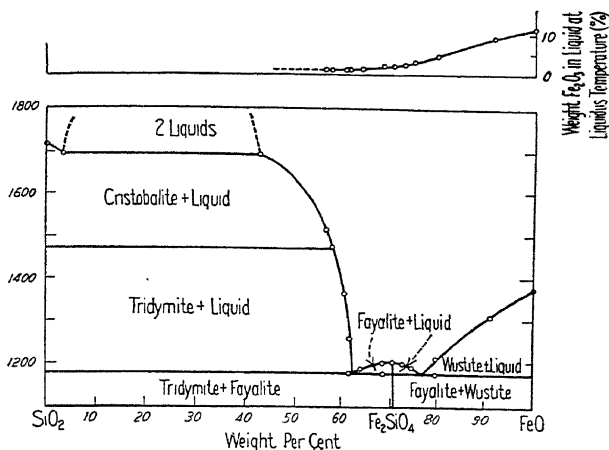


FIG. 213.

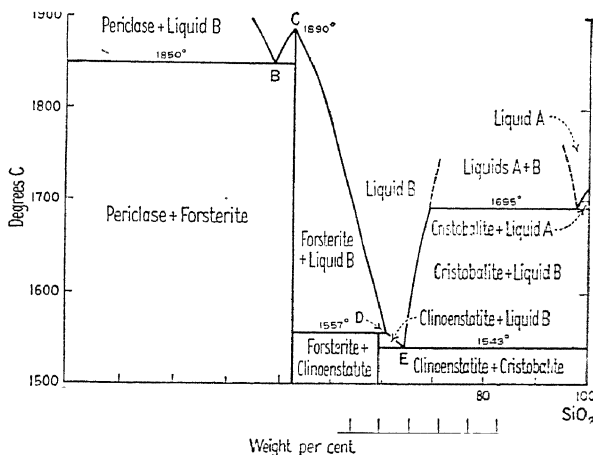


FIG. 214.

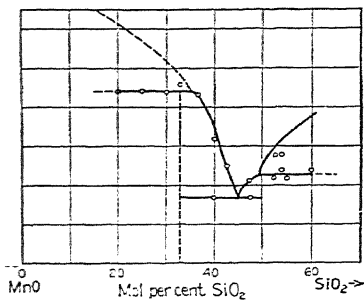


FIG. 215.

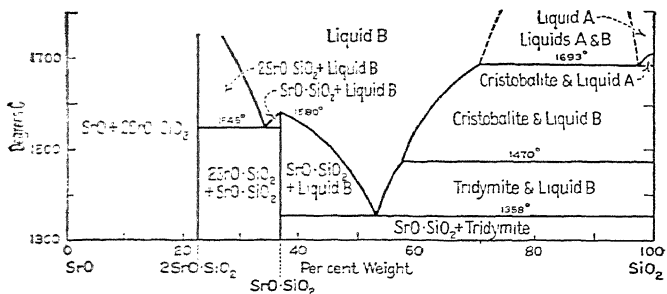


FIG. 216.

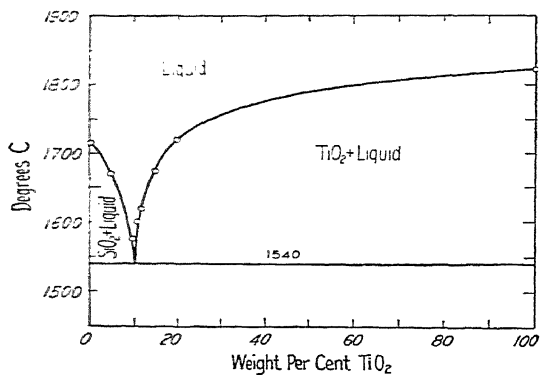


FIG. 217.

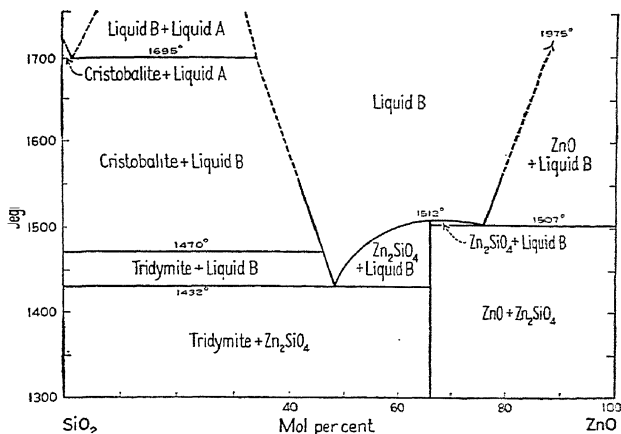


FIG. 218.

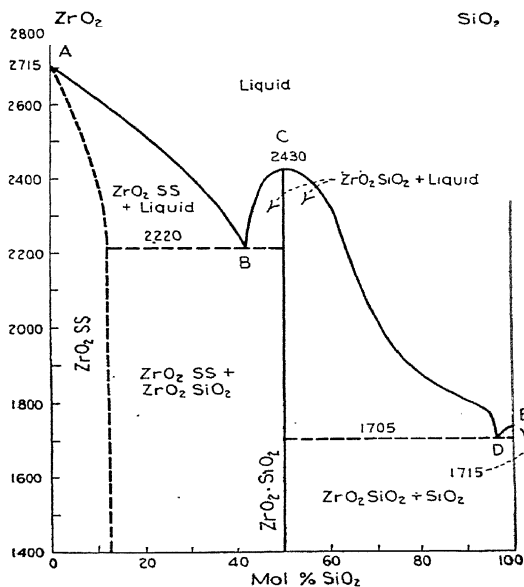


FIG. 219.

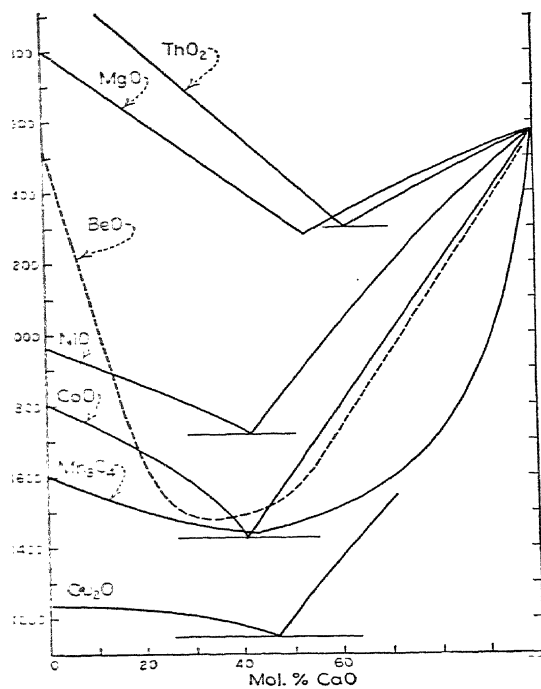


Fig. 220.

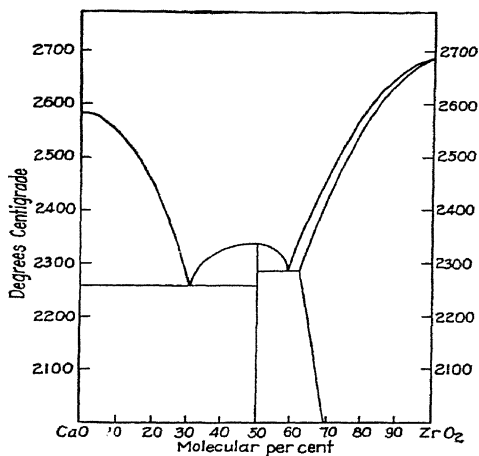
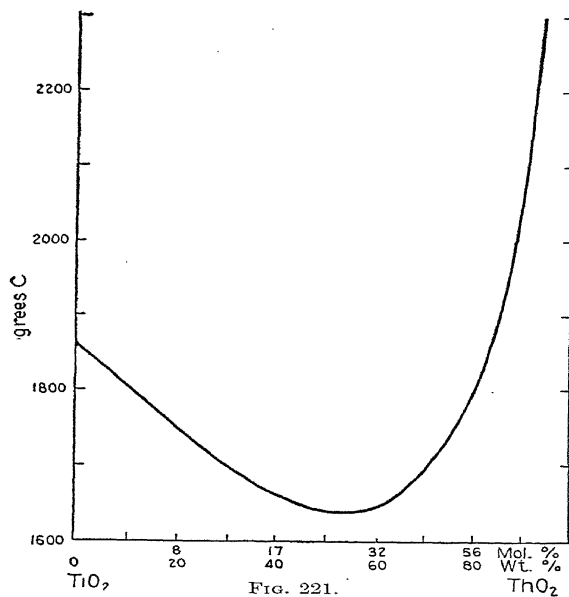


FIG. 222.

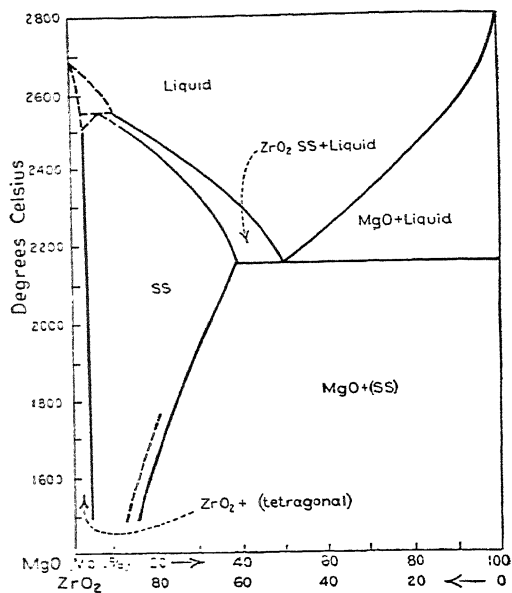


FIG. 223.

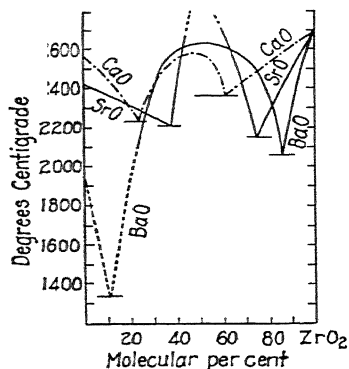


FIG. 224.

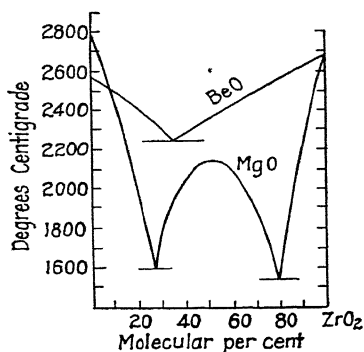


FIG. 225.

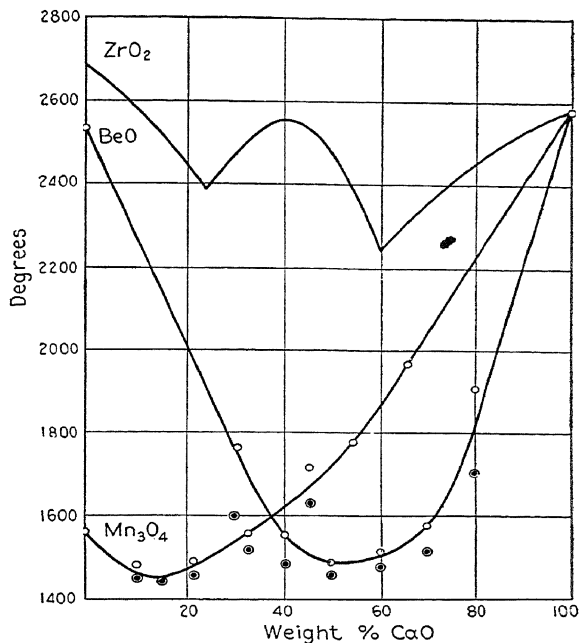


FIG. 226.

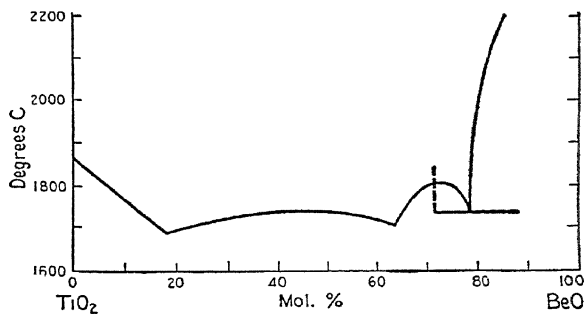


FIG. 227.

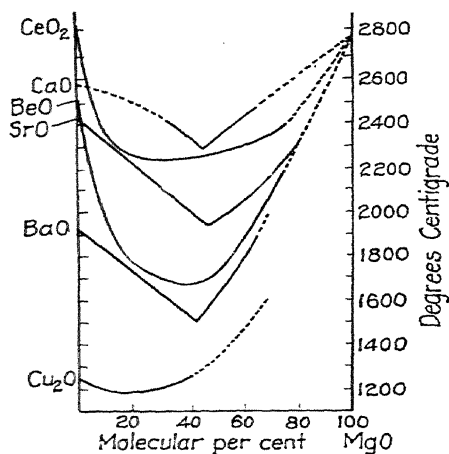


FIG. 228.

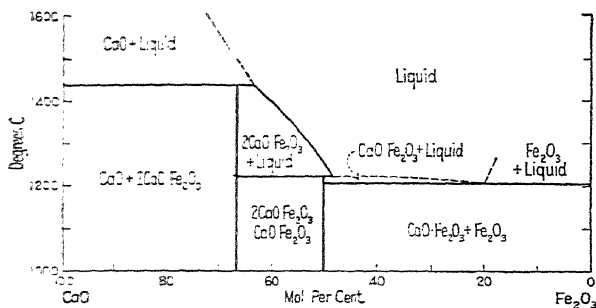


FIG. 229.

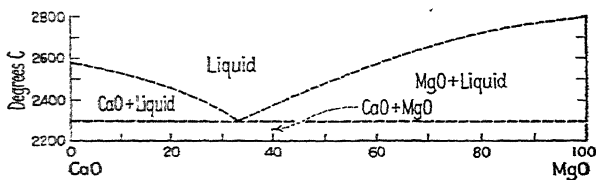


FIG. 230.—(Weight per cent.)

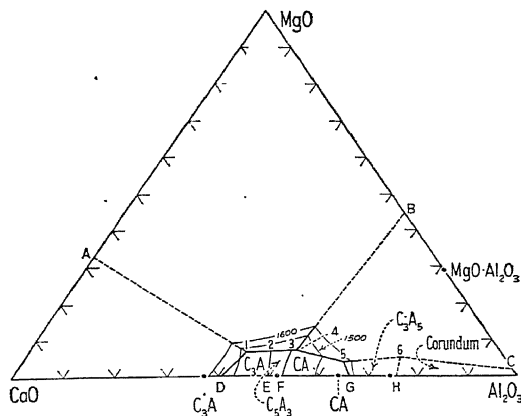


FIG. 231.—(Weight per cent.)

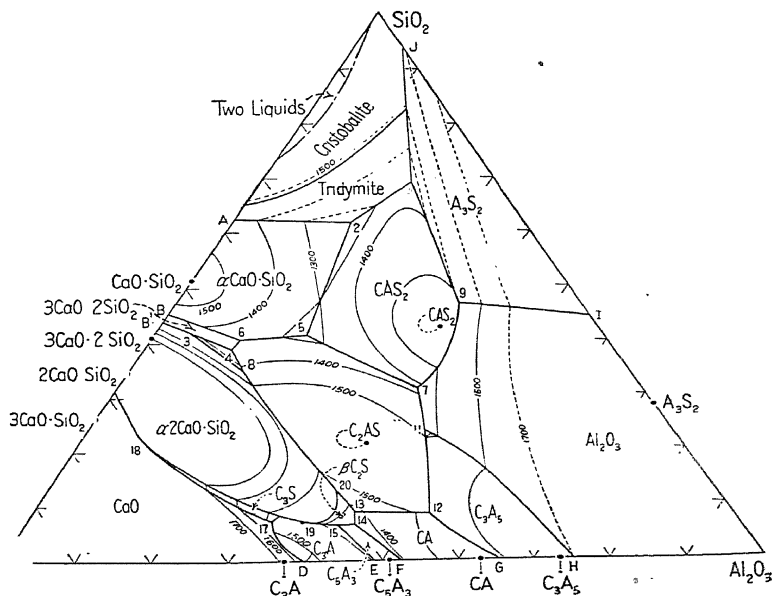


FIG. 232.—(Weight per cent.)

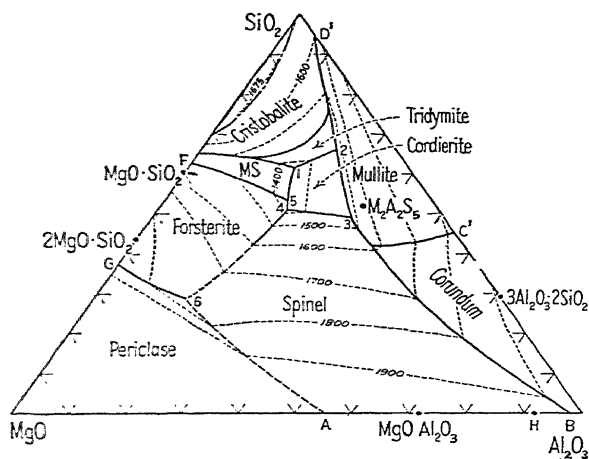


FIG. 233.—(Weight per cent.)

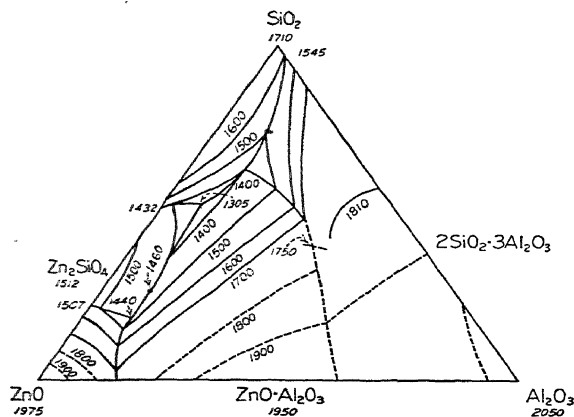


FIG. 234.—(Weight per cent.)

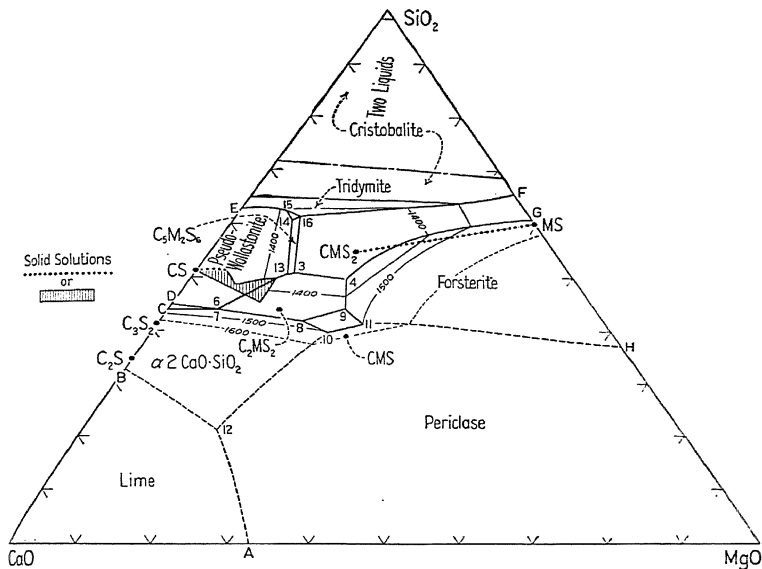


FIG. 235.—(Weight per cent.)

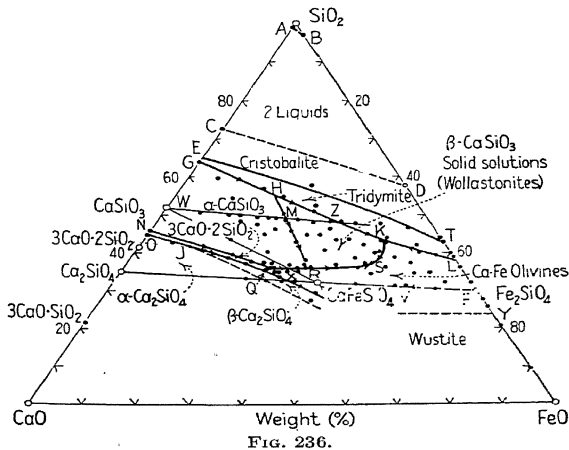


FIG. 236.

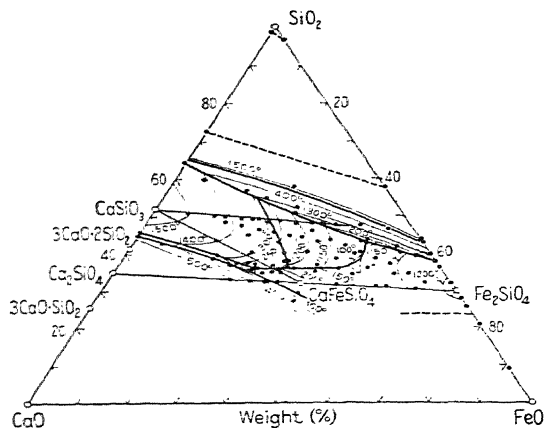


FIG. 237.

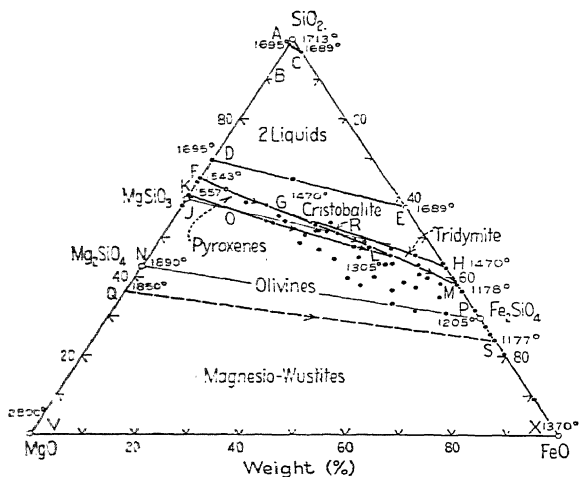


FIG. 238.

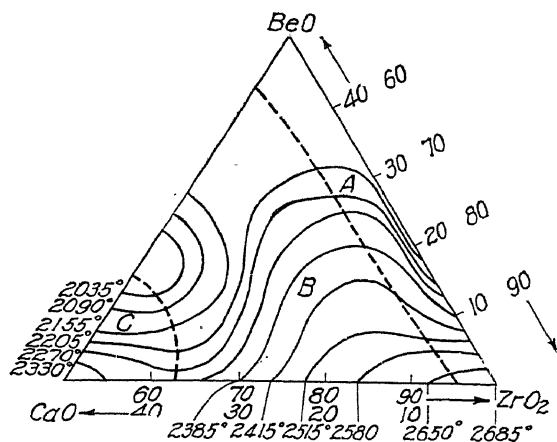


FIG. 239.—(Weight per cent.)

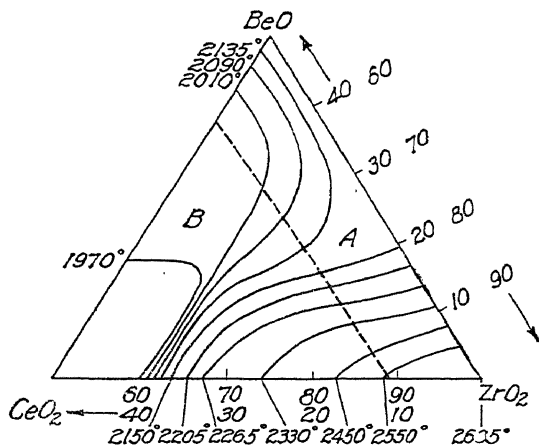


FIG. 240.—(Weight per cent.)

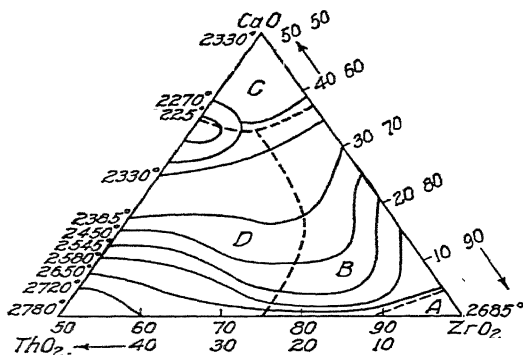


FIG. 241.—(Weight per cent.)

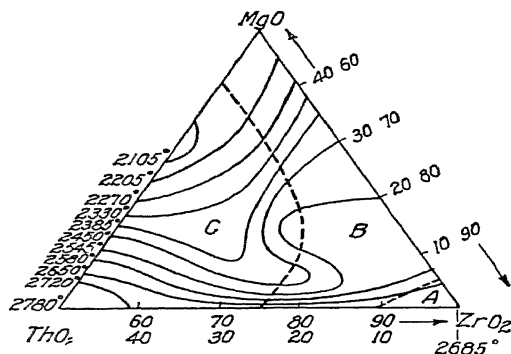


FIG. 242.—(Weight per cent.)

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CHAPTER XIII

LOAD-BEARING CAPACITY OF REFRACTORIES

1. Mechanism of Load Failure. *Flow Characteristics of Glass.*
The flow properties of a heated glass fiber are shown in Fig. 243, in which the elongation is plotted against time for a single load.

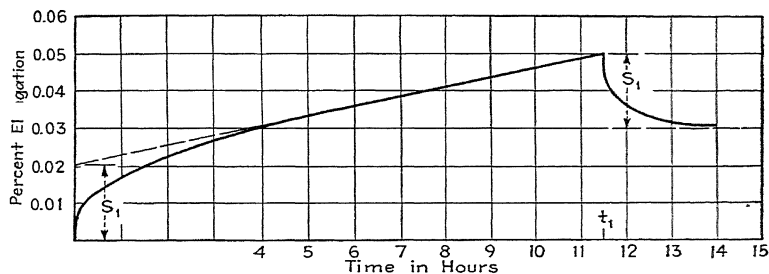


FIG. 243.—Flow of heated glass.

It will be noted that the flow starts in rapidly but soon decreases until it reaches a constant rate. If the straight portion of the curve is projected back to the zero time axis, the value S_1 is obtained which represents the elastic strain. If, at time t_1 , the load is removed, the glass will contract rapidly at first and then more slowly until it reaches a fixed length. The amount of contraction is equal to S_1 , or the original elastic effect. The heated glass is a truly viscous material; for if the steady rate of flow is plotted against stress as shown in A of Fig. 244, a straight line passing through the origin results.

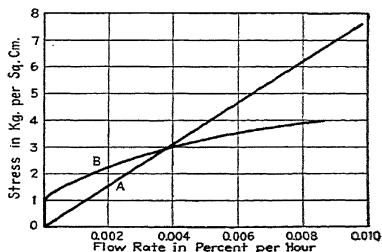


FIG. 244.—Flow characteristics of a viscous material (A) and an elastico-plastic material (B).

The mechanism of flow in glass can perhaps be made clearer by considering a mechanical model, the motion of which reproduces the glass flow with considerable exactness. This model, shown in Fig. 245, consists of the spring *A*, which represents the elastic effect in the glass but is restrained from reaching instant equilibrium by the dashpots *B*, representing the restraining force or internal friction of the glass. The steady flow of the glass is represented by the motion of the dashpot *C*; the weight *W* provides the extension force.

Flow of Crystals.—The flow of single crystals of nonmetals at elevated temperatures has not been studied with any great care.

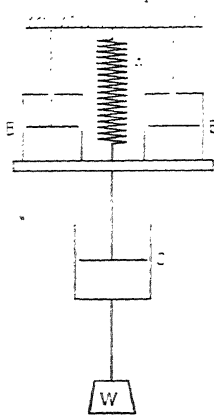


FIG. 245.—Model simulating the flow in glass.

It is believed that the single crystal has a definite yield point and is comparatively rigid close to the melting temperature. Research on single crystals is complicated by the fact that some distortion occurs, probably along the slip planes, until there is no longer a single crystal and we must consider the system as many similarly oriented small crystals. A still greater departure from a single crystal is a system of small crystals with random orientation, which gives, in effect, the conditions of an isotropic medium. Here again, we have little information on the flow properties but believe that the material is comparatively rigid up to the softening point.

Flow of a Mixture of Crystals and Glass.

This mixture, which is a normal characteristic of most refractory materials, has been studied to a considerable extent. Such mixtures are elasticoplastic materials, similar in flow characteristics to plastic metals; *i.e.*, if the steady rate of flow is plotted against stress, a line results that does not pass through the origin but indicates a certain minimum stress necessary to initiate flow, as shown in curve *B* of Fig. 244, a characteristic typical of all plastic materials. The time-elongation curve, however, is very similar to that for a glass, as indicated in Fig. 246 for a porcelain. This shows the initial portion of rapid flow and later the gradual conformity to a uniform rate. It is characteristic of almost all refractory mate-

rials that the rate of flow soon after the load is applied is much greater than after a uniform condition has been reached. Also it should be remembered that in plastic flow, the rate of flow is

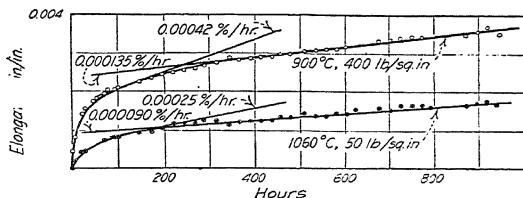


FIG. 246.—Plastic flow of heated porcelain.

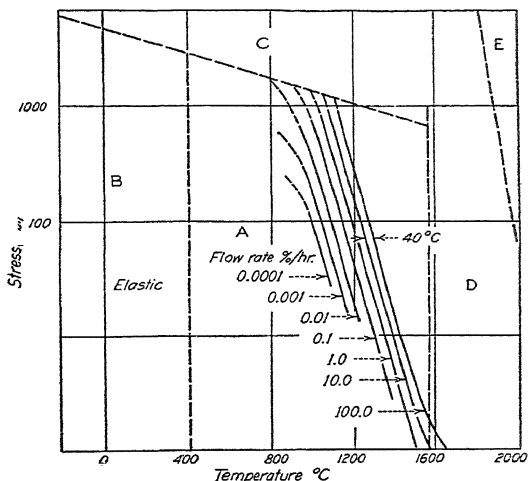


FIG. 247.—The flow field of a porcelain.

- A = field of plastic flow
- B = field of elastic flow
- C = field of instant breaking
- D = field of viscous flow
- E = field of turbulent flow

roughly proportional to the fourth power of the stress and not the first power as in viscous flow.

In Fig. 247 is shown a more or less idealized type of flow diagram for a refractory material at various temperatures.

The flow relations in an elasticoviscous material may be clarified by a mathematical discussion.

Let S_t = the total flow of the specimen

S_e = the elastic portion of the flow

S_1 = the total elastic flow under the external force F

Now the force acting at any instant to cause elastic flow is

$$F_1 = F(S_1 - S_e)$$

That is, at the start of flow, $F_1 = F$; whereas at the condition of equilibrium flow, $F_1 = 0$.

The retarding force restraining the elastic flow is given by

$$F_2 = k \frac{dS_e}{dt}$$

But at any time

$$F_1 = F_2$$

or

$$F(S_1 - S_e) = k \frac{dS_e}{dt}$$

Solving for S_e we obtain

$$S_e = S_1(1 - e^{\frac{Ft}{k}})$$

The viscous flow is

$$S_v = k_1 t$$

Then

$$S_t = S_e + S_v$$

$$S_t = k_1 t + S_1(1 - e^{\frac{Ft}{k}})$$

This expression represents the flow relation of Fig. 243 and the motion of the model of Fig. 245. After a period of time, the second term becomes zero and the flow is steady.

In the case of elastico-plastic flow, we can set up the expression for the elastic flow as

$$F(S_1 - S_e) = k_2 \left(\frac{dS_e}{dt} \right)^n$$

and for the plastic flow as

$$S_p = k_3 t$$

where S_p = the plastic flow

$n = 1.4$ (approximately)

The solution of these equations gives an expression for the total flow of

$$S_t = k_3 t + S_1 \left(1 - \sqrt[3]{\frac{1}{3F^4 S_1^3 + 1}} \right)$$

When gas or oil fuel is used, the furnace shall be of such form that the temperature is substantially uniform in all parts of the furnace. Two burners shall be used. These shall be capable of individual control and located to produce a tangential flame that will not impinge on the specimens or on the thermocouple protecting tubes.

b. The temperature shall be measured either with calibrated platinum-platinum-rhodium thermocouples, each encased in a protection tube with the junction not more than 1 in. (25 mm.) from the center of the side or edge of each specimen farthest from the center of the furnace, or with some form of pyrometer that has been calibrated against a thermocouple in the furnace. A recording form of temperature indicator is recom-

TABLE 58.—TIME-TEMPERATURE SCHEDULES FOR HEATING THE
TEST FURNACE

NOTE: All temperatures shall be maintained within $\pm 10^{\circ}\text{C}.$ of those prescribed in this table, and the averages of the temperatures attained shall equal those specified.

Temperatures for various heating schedules, $^{\circ}\text{C}.$,
fireclay brick

Hours	Minute	Schedule No. 3, super duty	Schedule No. 2, high heat duty	Schedule No. 1, intermediate heat duty
After 1	0	550	500	500
	15	680	620	595
	30	800	720	685
	45	900	815	770
After 2	0	990	900	850
	15	1070	980	920
	30	1140	1045	990
	45	1200	1100	1050
After 3	0	1250	1150	1100
	15	1290	1195	1145
	30	1330	1235	1185
	45	1370	1270	1220
After 4	0	1400	1300	1250
	15	1430	1330	1275
	30	1450	1350	1300
	45	1450	1350	1300
After 5	0	1450	1350	1300
	15	1450	1350	1300
	30	1450	1350	1300
	45	1450	1350	1300
After 6	0	1450 (end)	1350 (end)	1300 (end)

mended. If the optical pyrometer is used, observations shall be made by sighting into refractory tubes having closed ends and in the same relative positions to the test specimens as those specified for the thermocouples.

3. Test Specimen.—*a.* The test specimen shall consist of a minimum of two 9 by 4½ by 2½ in. straight refractory brick, or specimens of this size cut from larger shapes, utilizing as far as possible existing plane surfaces.

b. If necessary, the ends of the specimen shall be ground so that they are approximately perpendicular to the vertical axis.

c. The test specimen shall be measured before testing, four observations being made on each dimension (length, width, and thickness) at the center of the faces to within plus or minus 0.02 in. (0.5 mm.). The average dimensions shall be recorded, and the cross section calculated.

4. Setting the Test Specimen.—The test specimen, set on end, shall occupy a position in the furnace so that the center line of the applied load coincides with the vertical axis of the specimen as indicated in Fig. 247*a* and shall rest on a block of some highly refractory material, neutral to the specimen, having a minimum expansion or contraction. (Recrystallized silicon carbide brick have been found satisfactory for this purpose.) There shall be placed between the specimen and the refractory blocks a thin layer of highly refractory material such as fused alumina or silicon carbide, which has been ground to pass a No. 20 (840μ) A.S.T.M. sieve (equivalent to mesh No. 20 of the Tyler standard series). At the top of the test specimen a block of similar highly refractory material should be placed, extending through the furnace top to receive the load.

NOTE.—Gross errors which may more than double the deformation will result if the specimen is not set perpendicular to the base of the support or if the load is applied eccentrically.

5. Procedure. *a. Loading.*—The gross load to be applied shall be calculated from the average cross section of the original specimen as determined in Sec. 3*c*. A load of 25 lb. per sq. ft. (1.765 kg. per sq. cm.) shall be used.

b. Heating.—The rate of heating shall be in accordance with the requirements of Table 58 and the time-temperature curves shown in Fig. 247*b* which give the rate and time of heating required for different classes of refractory materials. The temperature shall not vary more than $\pm 10^{\circ}\text{C}$. from the specified temperature.

c. Furnace Atmosphere.—The furnace shall be operated with an oxidizing atmosphere above 800°C .

d. *Completion of Test.*—At the expiration of the time of heating, the supply of heat shall be stopped and the furnace allowed to cool by radiation to $1000^{\circ}\text{C}.$, or lower, before the load is removed and the specimens

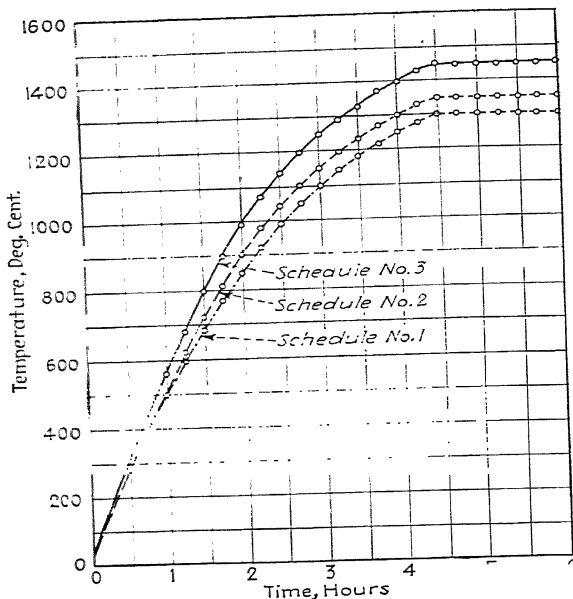


FIG. 247b.—Time-temperature curve for load test.

examined. When the test specimens have cooled to room temperature, they shall be remeasured for length in accordance with Sec. 3c, and the average deformation shall be recorded and reported to the nearest 0.5 per cent of the original length.

NOTE.—It is recommended that a photograph be made of the specimen before and after testing, since these will yield useful information.

The A.S.T.M. load test has been developed over a long period to fit best the needs of the manufacturer and the user of refractories and is particularly useful in control testing. As discussed later, it does not give information particularly suited to the need of the designer.

European Load Tests.—In Europe, the load test is generally carried out on smaller specimens, *i.e.*, cylinders approximately 1 in. in diameter and 1 in. high. This method is preferred because the temperature can be made more uniform over the

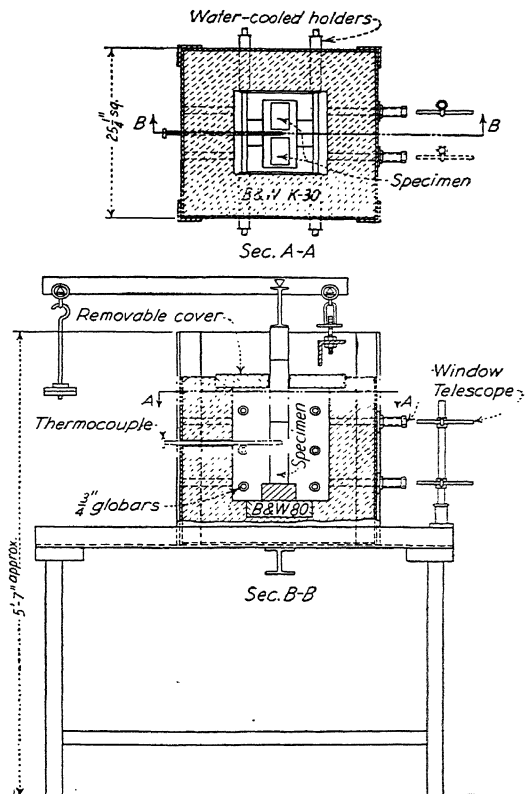


FIG. 248.—Electrically heated load test furnace. (*J. Am. Ceram. Soc.*)

specimen and the furnace is smaller and more easily controlled. On the other hand, such a small specimen may not represent accurately the structure of a coarse-grained brick, and the specimens are so short that the precision of measuring the elonga-

tion is somewhat less than with the larger specimens. However, there are certain advantages with each type of specimen; and

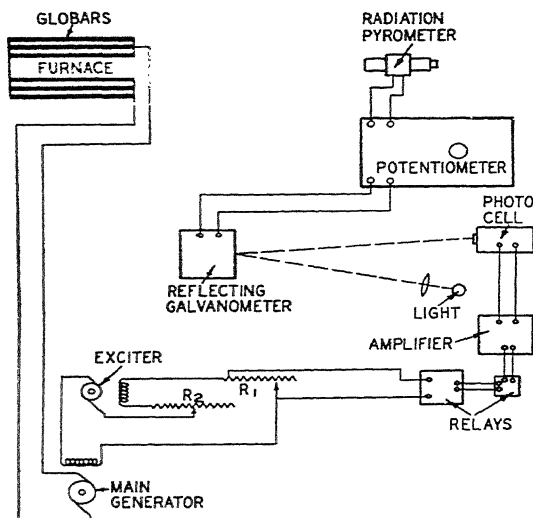


FIG. 249.—Controlling apparatus for long-time constant-temperature tests. (*J. Am. Ceram. Soc.*)

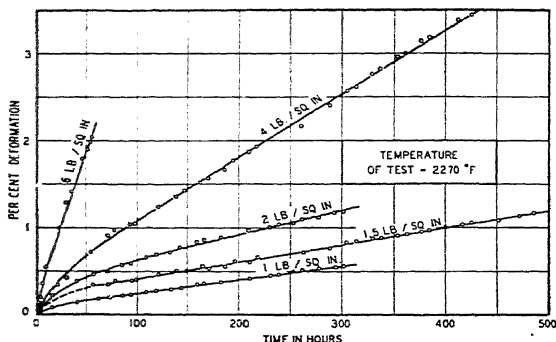


FIG. 250.—Time-elongation curve for a firebrick. (*J. Am. Ceram. Soc.*)

with carefully made tests, either should give reliable results. An excellent discussion of the load test is given in the references.^(36,37)

Long-time Creep Tests.—Recently, some work has been carried out on the load testing of refractories in the same way that creep tests are made with metals;^(45a) i.e., the refractory is heated to a uniform temperature and then loaded for a sufficient length of time to establish a uniform rate of flow. A furnace which is heated by electric globars to the necessary temperature for carrying out this test is shown in Fig. 248. As accurate temperature control is required for these long-time tests, the controlling apparatus shown in Fig. 249 has been developed which will give a control of $\pm 2^{\circ}\text{F.}$ for long periods of time. The length of the specimen not only is measured at the end of the run but is

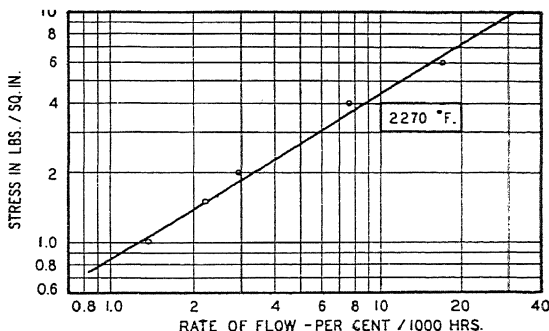


FIG. 251.—Flow rate vs. load. (*J. Am. Ceram. Soc.*)

measured every day with a pair of telescopes sighting on the ends of the specimen in order to determine a time-elongation curve. Figure 250 shows such a curve for a firebrick run in this way; and in Fig. 251, the flow rates are plotted against load on logarithmic paper. It is felt that for design purposes, the long-time tests are much to be preferred to the short-time tests previously described. Whether or not the shorter tests give accurate comparisons between various bricks cannot be determined until more long-time tests have been made to reproduce more nearly actual conditions.

3. Load Values for a Number of Refractories.—In Table 59 will be found the comparative load values for a number of fireclay brick that have been tested in the A.S.T.M. type load test as published by the Refractories Institute.

TABLE 59.—LOAD-BEARING CAPACITY OF FIRECLAY BRICK

Method of manufacture	Brand No.	Pyrometric cone equivalent	Subsidence, per cent, at 1350°C. (2462°F.) load test 25 lb. per sq. in.	Chemical composition					
				Silica	Alumina	Iron oxide	Titanium	lime and magnesia	combined alkalis
Dry press.	A	19	Failed	68.	24.03	2.57	1.24	0.92	2.01
	B	31	12.70	55.20	40.00	2.40	2.00	0.80	1.60
	C	32	3.40	61.18	35.05	1.91	1.04	0.61	0.71
	D	32	10.50	54.22	38.58	1.86	2.26	0.87	2.34
	E	32-33	3.60	54.08	40.97	2.34	1.89	0.40	1.42
	F	33	6.90	53.00	42.70	1.70	2.04	0.70	0.80
	G	33	2.60	52.47	42.70	1.56	1.97	0.48	0.62
Stiff-mud...	H	35-36	0.90	33.54	59.64	1.76	2.34	0.54	1.55
	I	31-32	1.30	73.81	21.69	1.85	0.90	0.40	0.66
	J	30-31	4.00	68.24	28.29	1.55	0.66	0.94	0.32
	K	30-31	5.60	60.04	33.22	1.83	0.99	1.20	2.32
	L	32-33	5.60	57.44	36.88	2.14	1.80	0.75	0.72
	M	32-33	3.90	52.66	38.57	2.28	2.53	0.	2.64
	N	32-33	1.85	52.73	43.20	2.29	1.02	0.44	0.37
Hand-made..		29-30	4.95	75.96	21.46	1.12	1.10	0.54	0.70
		27-28	2.62	70.00	25.00	1.20	1.00	0.50	2.80
		30-31	9.86	65.28	28.47	1.77	0.66	0.	1.79
		31-32	3.30	60.08	34.04	1.40	2.16	0.63	1.84
		32	8.43	48.42	44.33	3.58	1.70	0.90	1.52
		32	5.95	51.30	42.30	2.23	2.28	0.4	1.55
		33-34	10.90	42.20	49.98	3.18	2.40	0.85	1.47

Table 60 shows load values for a number of special refractories

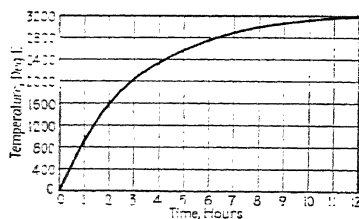


FIG. 252.—Load-test schedule for special bricks.

run in the A.S.T.M. furnace but at the schedule shown in Fig. 252 in order to bring all of them down to give a direct comparison.

Only recently⁽⁴⁶⁾ have any values been available on the load values of insulating firebrick. The bricks shown in Table 61 are representative of those on the market at present. Their load value together with those of two second-quality fireclay brick are given in Table 62 when heated on the schedule shown in Fig. 253. It is interesting to notice that some of the insulating firebrick, even though they have a porosity of around

80 per cent, give a resistance to load superior to the second-grade fireclay brick with a porosity of around 25 per cent.

4. Factors Influencing the Load-bearing Capacity of Refractories.—In general, it may be said that the load-bearing capacity of a refractory is directly influenced by the amount and viscosity of the glassy phase. Anything that can be done to diminish the amount of glass or raise its viscosity will increase the resistance

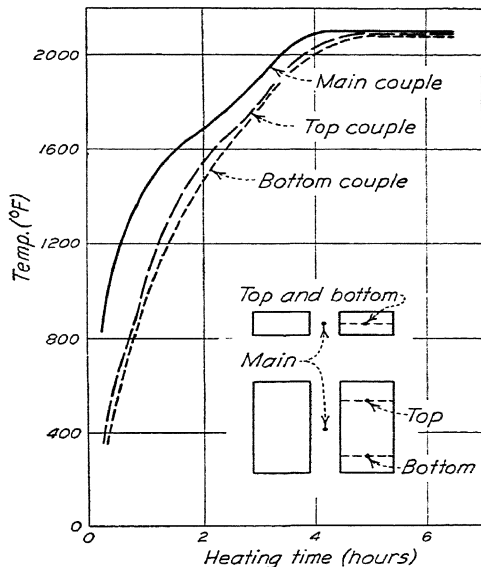


FIG. 253.—Temperature vs. heating time during load testing of insulating firebrick. (J. Am. Ceram. Soc.)

to flow. This may be accomplished by adding to the refractory a material that will form from the glass a more viscous material or a material containing more crystals. For example, a chrome brick containing silica as an impurity may have a comparatively low load value; whereas if the proper amount of magnesite is added to the brick, it will form the crystalline magnesium orthosilicate, forsterite, which will greatly increase the load-bearing value of the brick. Also, an increase in firing temperature will generally increase the load-bearing capacity because it distributes

TABLE 60.—SPECIAL REFRACTORIES

Type	Shrinkage			
	Began at		10 per cent at	
	°C.	°F.	°C.	°F.
Alumina (fused commercial)	1385	2525	1716	3121
Baddeleyite (baddeleyite bond)			(sheared at)	
	1560	2840	1613	2935
Baddeleyite (slay bond)	1232	2250	1376	2509
Cyanite	1415	2580	over	over
			1630	2970
Chrome (commercial)			(sheared at)	
			1404	2559
Kaolin	1385	2525	1593	2899
Magnesite (Grecian)			(sheared at)	
	1350	2462	1400	2552
Mullite (porous)	1552	2826	1727	3141
Mullite (vitreous)	None up to		1727	3141
Silica (commercial)			(sheared at)	
	1538	2800	1646	2985
Spinel			(sheared at)	
	1366	2491	1510	2750

TABLE 61.—TEST DATA ON COMMERCIAL INSULATING FIREBRICK

Brand No	Use limit, °F.	Weight, lb. per 9 in.-straight	Modulus of rupture, lb. per sq. in.	Cold crushing strength, lb. per sq. in.
A	2000	1.72-1.82	95	120
B	2000	2.21-2.75	197	172
C	2000	1.64	71	104
D	2000	2.27-2.32	107	559
O	2000	1.88	106	176
E	2200	1.87-1.96	165	193
F	2200	2.71-3.07	224	377
G	2200	2.27	129	208
N	2200	2.44	66	235
I	2500	2.40-2.63	196	248
J	2500	2.76	251	408
K	2600	2.30-2.50	133	128
L	2600	2.68-2.80	203	372
S	2600	2.40	127	196
M	2800	2.42-2.48	140	150
T	2900	2.90	235	220

the glassy phase more thoroughly and permits it to absorb crystallizing elements. This is shown in Table 63, which lists a number of commercial firebricks that were tested as they came from the kiln and then after refiring at a higher temperature.

TABLE 63.—EFFECT OF REBURNING ON THE LOAD-BEARING PROPERTIES OF FIREBRICKS

Brand No.	As received				After reburning to 1620°C.*			
	Shrinkage starts		10 per cent shrinkage		Shrinkage starts		10 per cent shrinkage	
	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.
A	1200	2192	1510	2750	1480	2696	1590	2894 S
B	1260	2300	1440	2624	1460	2660	1550	2822
C	1200	2192	1490	2714	1460	2660	1570	2858
D	1170	2138	1460	2660	1490	2714	1620	2948
E	1090	1994	1460	2660	1430	2606	1580	2876
F	1250	2282	1500	2732	1450	2642	1580	2876 S
G	1200	2192	1500	2732	1490	2714	1590	2894 S
H	1260	2300	1520	2768	1490	2714	1650	3002

* S indicates failure by shear. Load, 25 lb. per sq. in.

The structure of the brick also has some influence on the load-bearing capacity. For example, a brick of high porosity will have less load-bearing capacity than one of the same material with a lower porosity, as there is less material in the brick to carry the load in the latter case. It must be remembered, however, that the porous bricks are lighter and therefore do not need to carry a heavy load.

5. Application of Load-test Results to Design.—It will be clear from the preceding discussion that the results of the usual short-time load test are of little value to the designer of furnaces. Only with the long-time test that has come to equilibrium flow are values available for the designer to use in computing allowable stresses in the structure. From the curve in Fig. 251, the data may be utilized in the following example: A pier under the hearth of a heat-treating furnace has an allowable deformation of 10 per cent in its estimated working life of 4,000 hr., which amounts to a rate of 2.5 per cent in 1,000 hr. On the curve this corresponds to a loading of 1.7 lb. per sq. in.

It is probably safe to say that very few load failures occur in actual furnace construction and only in cases where the refractory part is heated all the way through, such as in piers, partition walls, and highly insulated crowns. Nearly all other parts of furnaces have a considerable temperature gradient from the hot to the cool side, and therefore the load is supported by a relatively cool portion of the refractory which is well able to carry the load. It is difficult with the data at hand at the present time to compute the load-bearing capacity of a wall with a variable temperature gradient, but an approximation can be made by dividing the wall up into a number of sections parallel to the face and considering the mean temperature of each section as a temperature for obtaining the load-bearing value. If these sections are all summed up, the load-bearing value of the whole wall can be roughly computed. It will be found, however, that in most cases, the cooler section will be responsible for supporting almost the whole load.

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CHAPTER XIV

SPALLING

Spalling is usually defined as a fracture of the refractory brick or block resulting from any of the following causes:

1. A temperature gradient in the brick, due to uneven heating or cooling, that is sufficient to set up stresses of such magnitude as to cause failure.
2. Compression in a structure of refractories, due to expansion of the whole from a rise of temperature, sufficient to cause shear failures.
3. Variation in coefficient of thermal expansion between the surface layer and the body of the brick, due to surface slag penetration or to a structural change in service, great enough to shear off the surface layer.

Many consider only the first type as true spalling. It is undoubtedly the predominating effect in refractories such as silica, magnesite, and chrome. As this type is caused by the inherent properties of the refractory, it offers a good opportunity for careful analysis. The second type of spalling is almost always due to poor furnace design, and the refractory itself can seldom be blamed. The third type can be minimized by using bricks burned higher than their subsequent operating temperature and by preventing slag penetration in so far as is possible.

The spalling properties of refractories cannot be consistently improved until we know the true mechanism of spalling. Although the study of stresses and fractures in brittle material is by no means well understood, light has been thrown on the matter in recent years. This work has been extended by Booze⁽¹¹⁾ and Phelps,⁽²³⁾ Green,⁽¹⁶⁾ Preston,⁽¹⁵⁾ numerous researches at the U.S. Bureau of Standards, and by Endell in Germany.

1. Temperature Stresses in Solids.—It may be of interest to examine first the distribution of stresses in an elastic solid when its surface is heated or cooled. It is rather surprising that there has been so little recognition of the difference in stresses resulting from heating as differentiated from cooling. As will be shown later, the stresses as well as the fracture are quite different in the two cases. An investigation, therefore, has been car-

ried out by the photoelastic method to determine the stresses occurring in various objects when suddenly heated and cooled at the surface.

Photoelastic Method.—The method of studying stresses in various structures by photoelasticity has recently been used to a considerable extent in determining the distribution of stress in objects where a direct computation is impossible. For example, valuable studies have been made of the stresses in hooks, eyebolts, ships' hulls, and gear teeth, although it is believed that very little work has been previously carried out on the measurement of temperature stresses by this method.

Photoelastic models must be made from a transparent isotropic medium. In this case, clear bakelite was selected because of its high stress-optical coefficient.

Polarized light is passed through a plane specimen, which becomes double refracting under stress and retards the two wave systems according to the values of the principal stresses p and q . The two wave systems interfere when passed through an analyzer and give isochromatic bands proportional to the difference $p - q$. The isochromatic lines are also lines of principal shear, for the principal shear stress at any point is equal to one-half the difference of the two principal stresses. The separate values of p and q may be determined by repeating the observations with circularly polarized light, which shows the isoclinic lines, or lines of equal direction of principal stresses. The values of p and q can be calculated from the isoclinic and isochromatic lines, the boundary conditions, and the constants of the material. It should be emphasized that this method applies only to a plane object.

Temperature Stress Tests.—The first model to be studied was a disk. This disk was carefully maintained at 50°C. (122°F.); then the circumference was suddenly heated to 100°C. (212°F.) by steam, and the resulting development of stresses watched until they had reached a maximum value, which required about 45 sec. The experiment was then repeated by suddenly chilling the circumference from 50°C. (122°F.) to 0°C. (32°F.) by means of ice water, and the stresses were similarly studied. In Fig. 254 are given the magnitudes and directions of the shear and resultant stresses under these conditions.

It will be observed that when the circumference is suddenly heated, tangential compression of considerable magnitude is

developed near the surface but the center of the disk is under a slight tension having an equal magnitude in all directions. The radial stresses are zero at the circumference but increase slowly toward the center. On the other hand, when the cir-

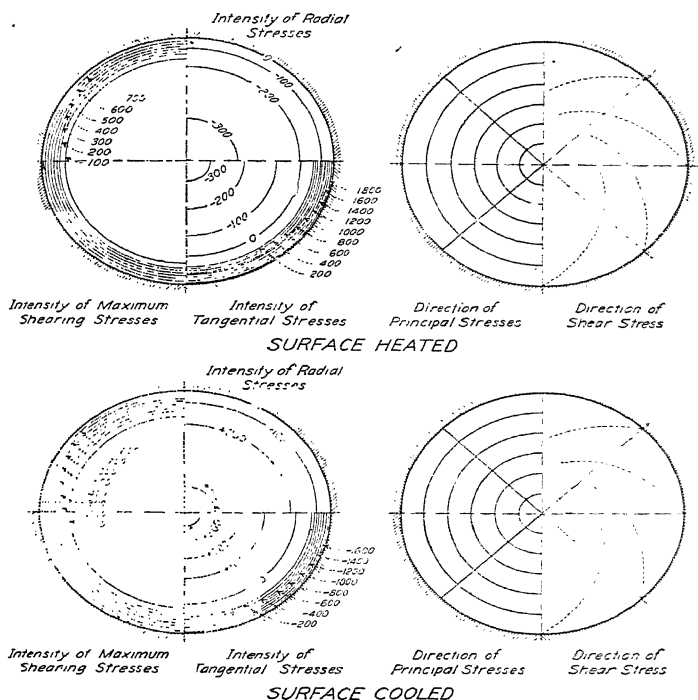


FIG. 254.—Stresses in a disk. (J. Amer. Ceram. Soc.)

cumference is cooled, the surface is under considerable tension and the center of the disk is under light compression. In both cases, the shear stresses are the same and reach a maximum at the circumference. Their direction is everywhere at 45 deg. to the radii.

The next model tested was a brick heated on the end. The stresses are shown in Fig. 255 in the same way as for the disk. On heating, a compression maximum occurred at the center

of the end; but on cooling, this was changed to a tension. It will be noted that the directions of the shear stresses are approxi-

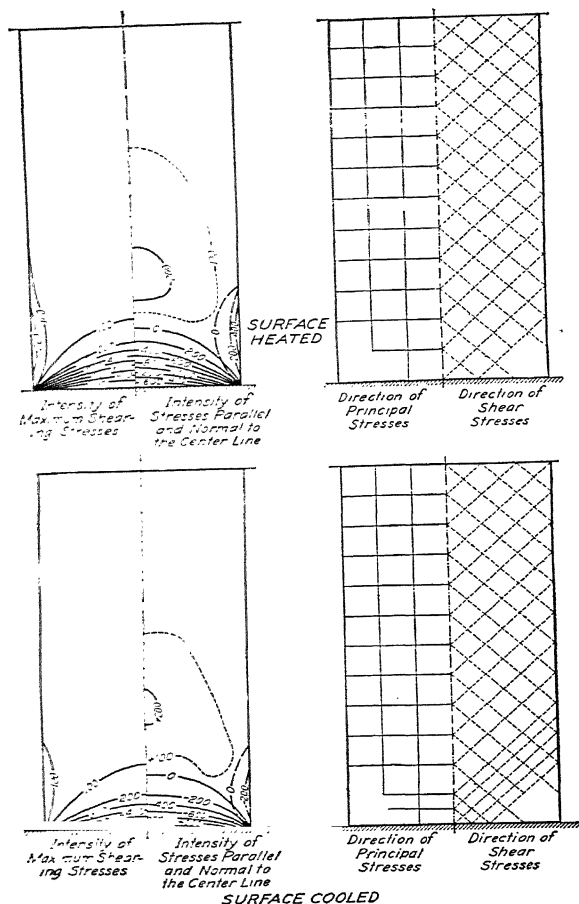


FIG. 255.—Stresses in a brick heated at one end. (J. Am. Ceram. Soc.)

mately 45 deg. to the surface everywhere and are a maximum at the center of the end.

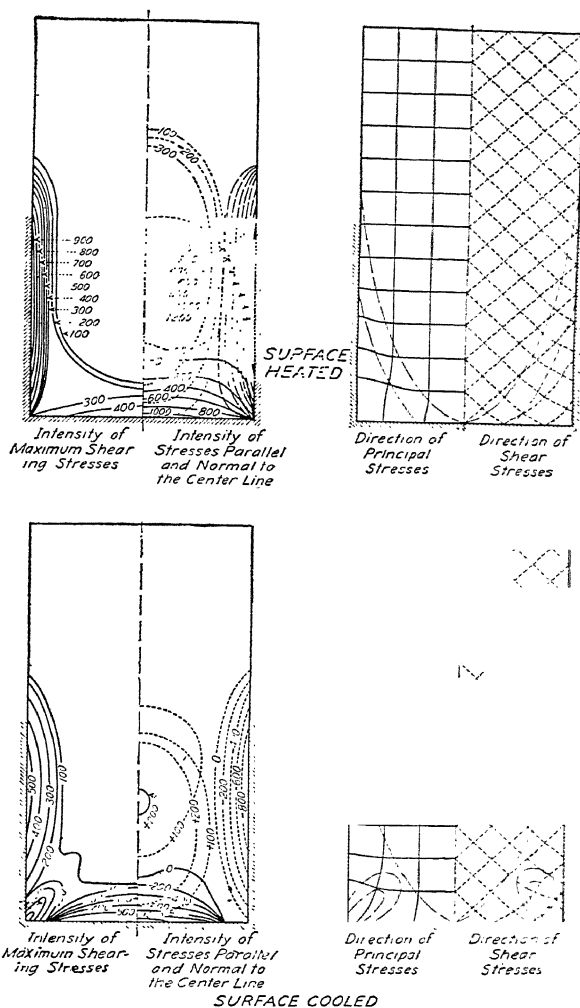


FIG. 256.—Stresses in a brick heated on one end and one-third of the distance up the side. (*J. Am. Ceram. Soc.*)

In the case shown in Fig. 256, the model brick was heated at the end and about one-third of the way up the side. A somewhat

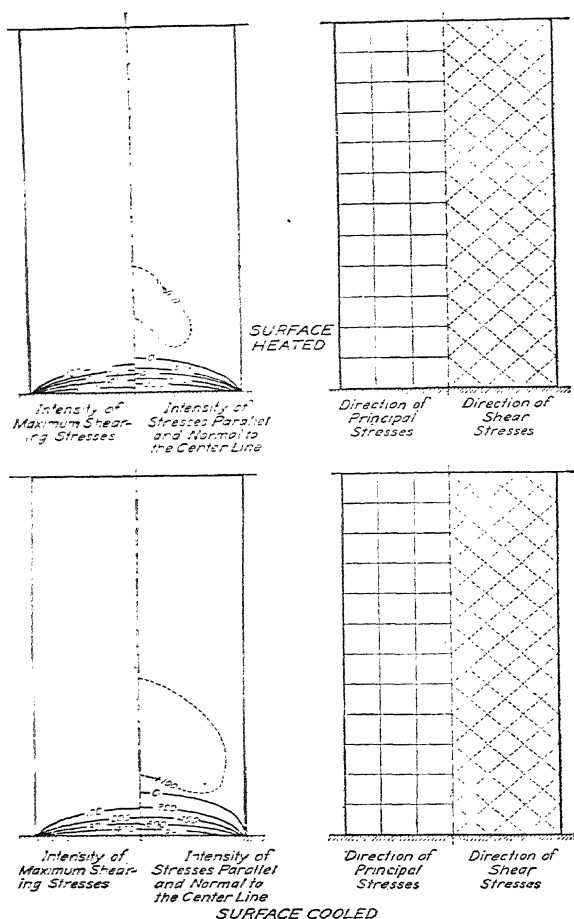


FIG. 257.—Stresses in a wall. (*J. Am. Ceram. Soc.*)

different type of stress distribution resulted, for the increase in stresses at the sides causes the stresses at the end to decrease.

It will be noted that at the corners, the shear lines are curved and follow the isothermals closely.

Figure 257 shows a model representing a brick in a wall when this wall is heated and cooled at the surface. The isothermals will then be parallel to the heated surface. It will be noted that the resultant normal stresses are nearly parallel and perpendicular to the surface of the wall and that the shear stresses are at 45 deg. to them.

Conclusions.—We may conclude from the preceding results that

1. The stresses set up in a solid by suddenly heating the surface through a certain temperature interval are of the same order but of opposite sign from those set up by cooling the surface through the same temperature range.

2. No high tensile stresses are developed on sudden heating.

3. The maximum shearing stresses are equal to one-half the maximum resultant stresses.

4. The stresses are generally low at the corners and interior of the specimen but reach their highest value along the heated sides at a distance from the corners.

2. Study of Cracks Developed in Spalling.—In order to correlate the types of cracks formed in the material when heated and cooled, with the stress distribution previously determined, a number of spheres and bricks were made up with a fine-grained, porcelain-like structure in order to make spalling occur readily. These objects were gradually heated to 900°C. (1652°F.) for the first condition and were placed in still air to cool. Under the second condition, the objects were heated by placing suddenly in a furnace that had a temperature of 900°C. (1652°F.).

Spheres.—Let us first consider the sphere that was suddenly cooled (Fig. 258). It will be noted that, in general, the fractures follow great circles. When the portions of the sphere were separated, it was noted that the cracks entered the surface in every case at approximately 90 deg. On the other hand, when the sphere is suddenly heated, a quite different type of fracture is obtained, as shown in Fig. 259. In this case, the fractures entered the surface at 45 deg. and tended to split off circular segments of the sphere having a height of approximately one-quarter the diameter.

Bricks.—Standard-size bricks were made up of the same material as the spheres. They were also heated and cooled in the same way. In Fig. 260 are shown the fractures resulting from rapid cooling. It will be noted that the fractures enter, in nearly every case, at right angles to the surface and tend to break the brick into cubes. Figure 261 shows the same brick when

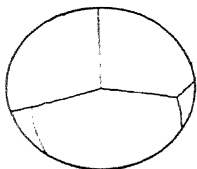


FIG. 258.—Cracks in a sphere suddenly cooled. (*J. Am. Ceram. Soc.*)

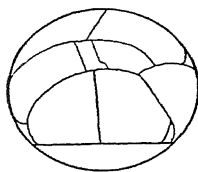


FIG. 259.—Cracks in a sphere suddenly heated. (*J. Am. Ceram. Soc.*)

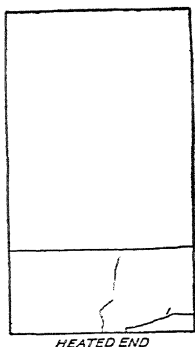


FIG. 260.—Cracks in a brick suddenly cooled. (*J. Am. Ceram. Soc.*)

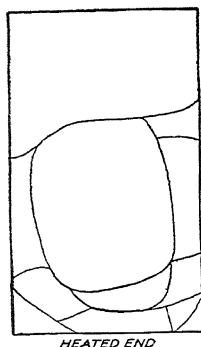


FIG. 261.—Cracks in a brick suddenly heated. (*J. Am. Ceram. Soc.*)

heated suddenly. The typical spalling failure is shown at the edges and corners; and in every case, cracks enter the surface at approximately 45 deg.

As a brick does not consist of a homogeneous material, it is possible to have a weakening or disintegration of the structure aside from actual fractures. This effect is usually due to a difference between the coefficient of thermal expansion of the

bond and that of the grog particles. This may be due to the use of different materials for the grog and bond or to a low-burned bond when the material is the same throughout. Goodrich⁽¹³⁾ has examined the loss in strength due to repeated heatings and finds a distinct weakening of the brick structure.

Conclusions.—We may conclude from the preceding studies that spalling is due to both shear and tension failures. On sudden heating, spalling is due almost entirely to shear stresses; and on sudden cooling, to tension stresses except at the corners and edges, where shear stresses may still cause failure. The shear values are about equal on heating and cooling, but there are no large tension stresses on rapid heating.

Shear failure occurs suddenly; *i.e.*, complete pieces are split off at each cycle of heating, and they begin to split at the edges and corners, so that a brick tends to approach a spherical shape on the end. The shear cracks follow in the lines of shear determined by the photoelastic method very closely, as is indicated by the slight curvature of the shear fractures at the corners.

Tension cracks seldom occur near the corners but usually first appear halfway up the brick where the tensile stresses are a maximum. The tension cracks enter the surface at 90 deg. They do not occur as suddenly, as do shear fractures, but penetrate deeper and deeper at each cycle until finally the cracks meet at the center. In every case, the tension failures follow approximately the lines of principal stress, although the deviation was considerably more than for the shear stress, owing undoubtedly to the length of the cracks and the greater influence of discontinuities.

It should be noted at this time that the stress distribution is much altered after a crack starts, as was pointed out by Preston.⁽¹⁵⁾ Generally, however, the tension cracks enter and leave at 90 deg. and shear cracks at 45 deg. to the surface. The fracture need not follow the direction of stress everywhere but will travel in such a way as to release the maximum strain energy. A great deal of confusion has been caused in the past by failure to differentiate between the effects of heating and cooling.

3. Theory of Spalling Due to Shear Stresses.—As shown in the preceding pages, a spalling failure may occur either by a shear or by a tension fracture. If we first assume a shear failure, which appears to be the most common type, it is possible to

analyze the mechanism of spalling in terms of the physical properties of the material.

Temperature Distribution.—It is necessary at first to consider the distribution of temperature in a homogeneous solid. We shall first make the assumption that this solid has one infinite plane surface. Originally this solid is at a uniform temperature of t_0 , but at time τ_0 the surface is suddenly cooled to a temperature of t_2 . The problem is to find the temperature distribution in the solid for different values of τ . For the solution, it will be necessary to apply Fourier's equation of heat flow. As the surface is infinite, the isothermal planes will be everywhere parallel to the surface of the solid. Putting $t_0 = t_1 - t_2$ or simply shifting the temperature scale, the temperature t at any distance below the surface x and at any time τ will be given by

$$t = \frac{2t_0}{\sqrt{\pi}} \int_0^{\frac{x}{2h\sqrt{\tau}}} e^{-\beta^2} d\beta \quad (1)$$

where h = a constant of the material

The diffusivity of a material, or the rate at which a point in a hot body will cool under definite surface conditions, is known as h^2 and is equivalent to $k/\rho c_p$, where k is the conductivity, ρ the density, and c_p the specific heat. It should be noted that the preceding equation is in the form of the probability integral and can therefore be readily evaluated from tables.

As will be shown later, the stress set up in a homogeneous material as a result of a change in temperature is proportional to the temperature gradient at any point. It will therefore be necessary to differentiate the preceding equation with respect to x .

We have

$$\begin{aligned} \frac{\partial t}{\partial x} &= \frac{2t_0}{\sqrt{\pi}} \cdot e^{-\frac{x^2}{4h^2\tau}} \frac{1}{(-2h\sqrt{\tau})} \\ &= \frac{-t_0}{h\sqrt{\pi\tau}} e^{-\frac{x^2}{4h^2\tau}} = \frac{dt}{dx} \end{aligned} \quad (2)$$

To show the practical application of this equation, curves have been plotted in Fig. 262 to give the temperature gradient $h = 0.080$ when a body is cooled suddenly from 850°C (1562°F.) to room temperature. The gradient is, of course, highest at the

surface but falls rapidly toward the interior. Near the surface, the gradient falls rapidly with increasing time; but at a certain depth, the gradient increases with the time. This is one of the reasons why spalling does not usually take place immediately after the specimen is chilled.

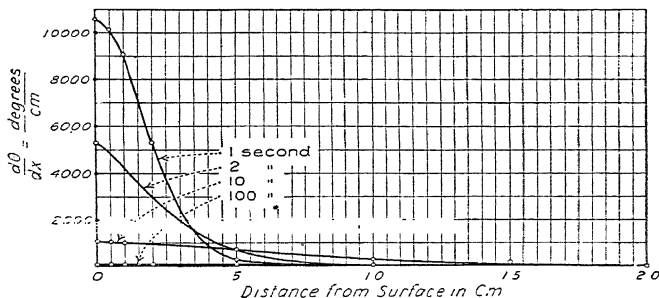


FIG. 262.—Temperature gradients at different levels below the surface of a cooling body. (*J. Am. Ceram. Soc.*)

In an actual case, the surface is not instantaneously cooled (1) because a cooling medium cannot be instantaneously introduced, and (2) because perfect thermal contact cannot be made between the cooling medium and the surface of the brick. The equations can be modified to take care of this effect, as suggested by Ingersoll and Zobel,⁽²⁾ by adding a fictitious distance beyond the true surface. In this instance, however, as we are not interested in the region very close to the surface, it will be more convenient to use a constant k to modify h .

Only the case of an infinite plane surface has been considered. At the edge of a solid, the isothermal planes will not be parallel to the surface but will be rounded off as in Fig. 263. This may be explained by considering that point A is cooled by the area abc in addition to the cooling received from an infinite surface such as a point at B . As the isothermals recede further from the surface, the area abc increases and corresponding departures from parallel conditions exist at corners.

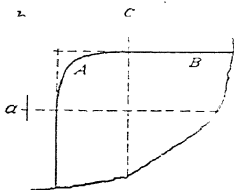


FIG. 263.—The rounding of isothermal planes at the edge of a solid. (*J. Amer. Ceram. Soc.*)

It is important to notice that the temperature gradient is slightly less at the edges and the corners than at the faces of a cooling brick; hence, corners spall off because of mechanical weakness rather than because of greater temperature gradients.

Temperature Stresses.—Now that we have the temperature distribution in a solid, it is possible to study the distribution of stresses. We shall first assume that the material is an elastic, homogeneous medium. It will be shown later that in the temperature range at which spalling occurs, the brick is perfectly elastic. The homogeneity will depend upon the structure of the brick and upon the process of manufacture.

The exact evaluation of the stresses in a brick under a given temperature distribution cannot be solved mathematically except

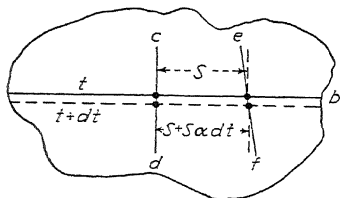


FIG. 264.—A portion of a heating or cooling brick. (*J. Am. Ceram. Soc.*)

in a few simple cases; however, it is required to find the tendency to spall only in terms of the physical properties of the material; *i.e.*, comparative but quantitative results are desired among various types of brick tested in the same manner.

Let us consider an isothermal plane ab in a portion of a heating or cooling brick at a given instant of time (Fig. 264). Let the temperature of the plane ab be t and that of another isothermal plane dx distant be $t + dt$, which gives the temperature gradient dt/dx . Let the plane cd cut the isothermal surfaces at a neutral point of shear. Now measure along ab a distance s , and erect the plane ef . If the temperature throughout the brick were t , this plane would be normal to ab ; but under the existing conditions, it will cut the $t + dt$ isothermal at a distance $s + \alpha \alpha dt$ from cd . The coefficient of expansion is α .

The shear strain is measured by the deflection of one plane with respect to another divided by the distance between them.

In this case,

$$\phi = \frac{s\alpha}{dx} \frac{dt}{dx} = s\alpha \frac{dt}{dx} \quad (3)$$

This means that the strain set up in a heating or cooling body is proportional to the size, the coefficient of thermal expansion, and the temperature gradient. This explains why large glassware cracks on cooling or heating more readily than small ware. In large pieces of refractory ware, the temperature distribution may be so uneven that strict proportionality to s may well be doubted. This does not greatly concern us, for we shall compare specimens of the same shape and size and with the same temperature gradient. The shear fracture theoretically should occur at 45 deg. to the isothermal but often is parallel to it. However, the direction of fracture does not affect the reasoning.

The shearing stress at any point is

$$f = \phi n \quad (4)$$

where n = the coefficient of rigidity

From Eq. (2),

$$\frac{dt}{dx} = \frac{k_1}{h} \quad (5)$$

where k_1 = a constant

This follows, for dt/dx is closely proportional to $1/h$ because small changes of h in the term $e^{-\frac{x^2}{4h^2\tau}}$ have little effect when τ is reasonably large.

Then the tendency to spall S_s is

$$\frac{f}{f_b} = \frac{\phi n}{f_b} = \frac{s\alpha \frac{dt}{dx} n}{f_b} = \frac{s\alpha \frac{k_1}{h} n}{f_b} \quad (6)$$

where f_b = the shearing strength

But for brittle materials,

$$n = \frac{f_b}{\phi_b} \quad (7)$$

where ϕ_b = the maximum shearing strain, or flexibility

Therefore, from Eqs. (6) and (7),

$$S_s = k_1 \frac{s\alpha}{h\phi_b} = k_2 \left(\frac{\alpha}{h\phi_b} \right) \quad (8)$$

This shows that the spalling tendency of a brick is proportional to the coefficient of thermal expansion divided by the square root of the diffusivity and maximum shearing strain.

4. Theory of Spalling Due to Tensile Stresses.—The preceding theory has been based entirely on the shear failure of a material under shear stresses. It was seen that this failure would occur on sudden heating of the brick. The sudden heating produces local compressive stresses in the material since the portion at a higher temperature tends to try to expand, but this being prevented by the cooler portions places the hotter portion of the brick in compression. It is known that brittle materials fail in shear when subjected to compressive stresses; hence, we get a shear failure under these conditions.

If the brick is suddenly cooled, a different phenomenon is involved. When one portion of the brick is suddenly cooled

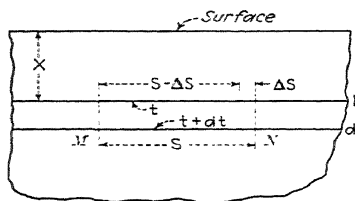


FIG. 265.—Illustration of tensile stresses in a heating or cooling brick.

below the temperature of the adjacent material, the part of the brick at the lower temperature tends to contract, but this contraction is prevented by the adjacent portions which are at a higher temperature. In this case, tensile stresses are set up in the cooler portion; and since

the shearing strength of a brittle material is usually considerably greater than the tensile strength, the brick will fail in tension, provided sufficiently rapid local cooling is present.

Let us then visualize a portion of the brick as shown in Fig. 265, which we will assume to be at the uniform temperature t_0 . This means that at the start, the isothermal planes ab and cd , which are initially separated by the distance dx , are at the same temperature t_0 . The surface of the brick is now cooled to a temperature t_2 ; and at a later time τ , the planes ab and cd possess temperatures t and $t + dt$, respectively, where the temperature is given by Eq. (1). Let us consider a gage length s between points M and N on plane cd . As a result of the lower temperature on plane ab , the material on this plane tends to contract by an amount Δs . This contraction is, however, prevented by the adjacent material, and a tensile strain is set up in plane ab of amount

$$\Sigma = \frac{\Delta S}{S} = \alpha \cdot dt \quad (9)$$

where α = the coefficient of thermal expansion

Now, from Eq. (5)

$$\frac{dt}{dx} = \frac{k_1}{h}$$

and

$$\sigma = E \cdot \Sigma \quad (10)$$

It follows from the preceding equations, then, that

$$\sigma = E \cdot \alpha \cdot dt = E \cdot \alpha \cdot \frac{k_1}{h} \cdot dx \quad (11)$$

If σ_b is the breaking stress of the material or the so-called "tensile strength,"

$$\sigma_b = E \cdot \Sigma_b \quad (12)$$

where Σ_b = the tensile breaking strain

The tendency to spall then becomes

$$S_t = \frac{\sigma}{\sigma_b} = \frac{E \cdot \alpha \cdot k_1 \cdot dx}{Eh \Sigma_b} = k_1 \cdot dx \frac{\alpha}{h \Sigma_b} \quad (13)$$

It will be noted that Eq. (13) has the same units and is in the same form as Eq. (8) of the preceding section. Instead of the shear strain ϕ_b at fracture, we have the tensile strain Σ_b ; and in place of the distance S from the neutral place of shear, we have the distance dx over which the temperature drop dt exists.

Let us now compare this equation with the Winkelmann-Schott⁽¹⁾ equation which is as follows:

$$\sigma = - \frac{A' A''}{A} \cdot \frac{t_0 \cdot E \cdot \alpha x}{2h \sqrt{\tau}} \quad (14)$$

where A' , A'' , A = constants

t_0 = the temperature of the outer layer

The tendency to spall is

$$S'_t = \frac{\sigma}{\sigma_b} = - \frac{A' \cdot A'}{2Ah \sqrt{\tau}} \frac{t_0 \cdot \alpha \cdot x}{(\sigma_b/E)} \quad (15)$$

or

$$S_t = k_3 \cdot x \cdot \left(\frac{\alpha}{h \bar{S}_b} \right) \quad (16)$$

where

$$k_3 = - \frac{A' A'' t_0}{2A \sqrt{\tau}} \quad (17)$$

It is thus seen that the Winkelmann-Schott equation can be put in the same form as given by Eq. (8) or (13). In the derivation given in the original article by Winkelmann and Schott, the size factor x was absorbed in another constant B , where B is essentially Kx . This, of course, can be done, since the purpose was to compare the spalling properties of various glasses for the same values of τ and x .

5. Experimental Confirmation of Theory.—In order to determine the validity of the equation for tendency to spall, the physical characteristics of a number of different bricks were tested and the tendency to spall, as computed from the preceding

TABLE 64.—CHARACTERISTICS OF BRICK TESTED FOR SPALLING

Material	Grog	Bond	Hardness	Approximate burning temperature		Remarks
				°C	°F	
A. Fireclay.....	Very coarse	Soft	Soft	1200	2300	Commercial brick
B. Silimanite.....	Medium	Little	Hard	1680	3050	Special brick
C. Fireclay.....	Very coarse	Soft	Medium	1430	2600	Same as A (hard burn)
D. SiC.....	20-mesh	Molasses	Hard	1540	2800	Special brick
E. Fireclay.....	Coarse	Soft	Soft	1316	2400	Commercial brick
F. Bauxite.....	Fine	Little	Hard	1704	3100	Special brick
G. Fireclay.....	Medium	Soft	Soft	1316	2400	Commercial brick
H. Kaolin.....	Medium	Little hard	Very hard	1650	3000	Commercial brick
I. Fireclay.....	Fine	Soft	Soft	1200	2300	Commercial brick
J. Fireclay.....	Medium	Hard	Hard	1200	2300	Commercial brick
K. Fireclay.....	Fine	Soft	Soft	1200	2300	Commercial brick
L. Spinel.....	Medium	Hard	Hard	1370	2500	Commercial brick
M. Silica.....	Fine	None	Hard	1480	2700	Commercial brick
N. Same as C pre-heated to 2900°F						

formula, was compared with the actual spalling characteristics of the brick.

Flexibility in Shear.—In order to measure the characteristics of the bricks as listed below, a number of $1 \times 1 \times 9$ -in. bars were sawed out of each specimen. These bars were then cemented into holders, and the angle and torque measured up to the breaking point at a temperature of 500°C . (932°F .).

Such a low temperature is justified because it has been noticed that spalling nearly always occurs at about red heat. In all cases where the specimen was carefully held, there was no permanent set after removing the torque until a point was reached just before failure; *i.e.*, the specimens all acted as if perfectly elastic. The bricks tested are described in the table below and represent a wide range. Some are experimental bricks; others are of extensively used commercial brands.

The Coefficient of Expansion.—The coefficient of thermal expansion of each type of brick was measured at 500°C . (932°F .). In general, the brick having the greatest coefficient of thermal expansion had the highest content of silica, but we are by no means justified in using the silica content of a brick as an index of its coefficient.

Diffusivity.—The value of the diffusivity can, of course, be obtained by measurements of thermal conductivity and specific heat. These measurements, however, are laborious and slow; so a simple method of measuring the relative diffusivity was devised. A 2-in. cube of the material was cemented from four $1 \times 1 \times 2$ -in. blocks with a thermal junction at the center; was suspended by the junction wires in an electric furnace until it had reached a constant temperature of about 550°C . (1022°F .); and then was taken out and suspended in a room free from drafts. The temperature of the center was recorded, and the slope of the cooling curve at 500°C . (932°F .) taken as the value for the diffusivity. This method is rapid and accurate where only relative values are desired.

The values of the diffusivity given are entirely arbitrary, and the results are comparable only among themselves, but it will be noted that with the exception of the silicon carbide specimen, the values of h vary only a few per cent and cannot be an important factor in spalling.

Comparison with Actual Spalling Tests.—The results from laboratory air-spalling tests are also given. A comparison between this test and actual service results has been made, and the agreement is generally good. From five to ten bricks of each kind were spalled, and the average taken.

Attention should be called to the two values given for bricks *B* and *F*. These two bricks showed the common type of shear spalling at the corners for several quenches, then suddenly broke across the center with a tension failure. The first value in the table gives the quenches actually obtained, and the

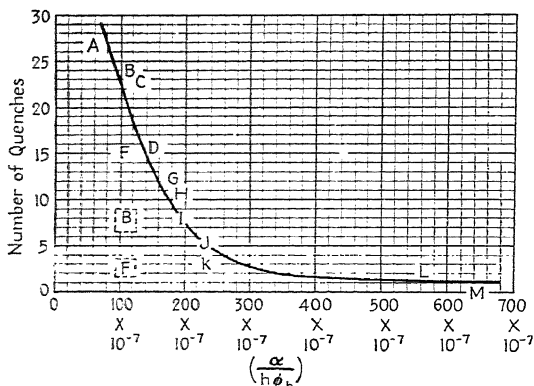


FIG. 266.—A plot showing correlation between theoretical and experimental values of spalling. (*J. Amer. Ceram. Soc.*)

second is estimated from the amount lost by shear. The first values have been disregarded in drawing the curves.

If the value of $\alpha/h\phi_b$ is an index of the spalling tendency of a brick as indicated by the theory, then these values plotted against the number of quenches for each specimen should fall along a curve rather than be widely scattered. Such a plot has been made in Fig. 266, and it is quite clear that the points group themselves into a definite band. The deviations that occur can be explained by the fact that some of the bricks were altered from their original characteristics in heating.

Specimen *K*, which is considerably below the mean curve, was noticeably laminated in structure. The higher values for bricks *B* and *F* were only estimates.

TABLE 65.—CONSTANTS FOR THE BRICKS TESTED

Brand	ϕ_b	α	h	$(\alpha/\phi_b h)$	Number of quenches
A.....	0.114	0.0000051	6.2	72×10^{-7}	26.5
B.....	0.052	0.0000039	6.5	115	8.0
B.....	0.052	0.0000039	6.5	115	24.0
C.....	0.050	0.0000050	6.3	157	23.0
D.....	0.072	0.0000031	9.9	44	*
E.....	0.057	0.0000053	6.5	143	15.6
F.....	0.032	0.0000037	6.2	110	2.0
F.....	0.032	0.0000037	6.2	110	15.0
G.....	0.090	0.0000104	6.2	187	12.2
H.....	0.050	0.0000063	6.4	197	10.6
I.....	0.107	0.0000133	6.3	197	8.4
J.....	0.050	0.0000071	6.0	237	5.2
K.....	0.089	0.0000126	6.2	229	2.7
L.....	0.032	0.0000116	6.4	567	2.4
M.....	0.094	0.0000405	6.7	644	0.3
N.....	0.060	0.0000072	6.1	197	

* No exactly comparable spalling value was available for this brick; but it is undoubtedly lower than should be expected, as an oxidizing atmosphere tends to convert the SiC into SiO₂ and thereby to raise the coefficient of thermal expansion.

The form of the curve is of interest, for it approaches a rectangular hyperbola asymptotic to the two axes. When the value of $\alpha/\phi_b h$ is high, the bricks show little difference in spalling resistance, as they are almost completely shattered at the first temperature change. On the other hand, the bricks having a low value of $\alpha/\phi_b h$ increase rapidly in spalling resistance as $\alpha/\phi_b h$ is decreased. This behavior is not unexpected, as it is simply an approach to a classification of bricks into two sets: those which spall on the first quench and those which do not spall under an infinite number of quenches.

The best spalling brick of those tested withstood 26 quenches and had a value for $\alpha/\phi_b h$ of 72×10^{-7} . Suppose that by slightly increasing the flexibility or by decreasing the coefficient of thermal expansion, a value of 50×10^{-7} were obtained; the brick should then withstand about 50 quenches. This illustrates the possibilities of making remarkable nonspalling brick.

On the whole, it would seem that the theoretical work agrees with practice as closely as the nature of the tests allows. Although this method cannot be recommended to replace the usual spalling

tests without a more thorough trial, it is felt that more information is obtained by it as to the causes of spalling in a certain brick than by other methods.

It is interesting to note that Booze⁽¹¹⁾ and Phelps⁽²³⁾ independently came to the same conclusions after testing a number of experimental bricks for coefficient of thermal expansion, diffusivity, and flexibility. They found that the best spalling bricks had the greatest flexibility and that the diffusivity had no appreciable effect. Endell's²⁶ work on magnesite brick checks this theory.

6. Laboratory Spalling Test.—The expense and the time required to determine the spalling characteristics of bricks in service are so great that a laboratory spalling test is highly desirable.

A number of spalling tests have been suggested and used. In most cases, they consist in subjecting the brick to a severe thermal shock in order that the test may produce definite results in a reasonably short time. Tests on single bricks, as formerly used, have now been almost abandoned, as they do not in all cases correspond to service conditions. Therefore the present A.S.T.M. test on a panel will be described. It is quite satisfactory but requires expensive equipment.

PANEL TEST FOR RESISTANCE TO THERMAL AND STRUCTURAL SPALLINGS OF REFRACTORY BRICK

A.S.T.M. Designation: C 38-42¹

ADOPTED, 1936;² REVISED, 1942

This Standard of the American Society for Testing Materials is issued under the fixed designation C 38; the final number indicates the year of adoption as standard or, in the case of revision, the year of last revision.

1. Scope.—This method of test is intended to show the resistance of refractory brick to the separate and combined effects of structural and thermal spalling. The test is believed to give a sufficient simulation of service conditions to suggest its use as a suitability test for certain classes of service that have been correlated with the test data (see NOTE).

NOTE: Such correlation is now available in the case of high-heat-duty clay brick for stationary boilers, malleable iron furnace bungs, and incinerator furnaces.

¹ A.S.T.M. Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

2. **Apparatus.**—The following apparatus and equipment¹ are needed:

a. *Panel Frame.*—A panel framework shall be used which is essentially the same as that shown in Fig. 266a.

b. *Preheating Furnace.*—A preheating furnace shall be used, constructed essentially like the design shown in Fig. 266b.

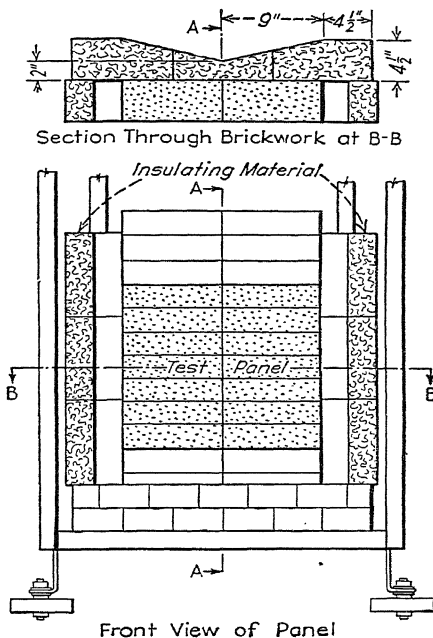


FIG. 266a.—Panel frame and brickwork. The brick around the test panel are dummy brick which are used to help maintain uniform conditions within the panel.

c. *Spalling Furnace.*—A spalling furnace shall be used, constructed in a manner as shown in Fig. 266c.

d. *Temperature-measuring Instruments.*—The temperature of the test panel during the preheating shall be measured by means of an optical pyrometer. The spalling furnace temperature shall be determined by means of a platinum, platinum-rhodium thermocouple.

¹ The complete set of drawings necessary for the construction of the panel spalling equipment would require too much space to be included with the procedure, but these are available at a nominal charge from the Refractories Fellowship, Mellon Institute of Industrial Research, Pittsburgh, Pa.

c. *Air Supply*.—Means shall be provided for delivering air through each cooling unit at a specified rate.

f. *Transfer Facilities*.—A suitable means, such as a track or trolley, shall be provided for transferring the test panels.

3. *Test Specimen*.—Whenever possible, the panel test specimen shall consist of 9-in. straight brick. When shapes of other sizes are to be tested, these shall be cut so as to be not more than 3 in. in thickness by 9 in. in length by $4\frac{1}{2}$ in. in width.

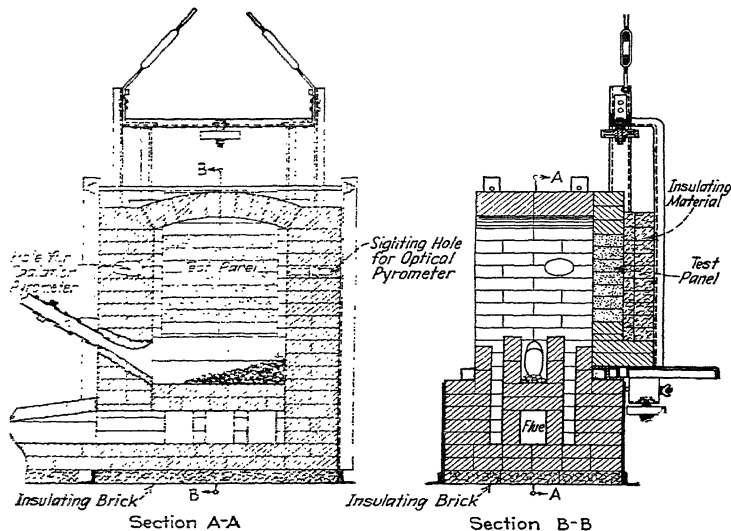


FIG. 266b.—Design of preheating furnace. In section *BB* there is shown in position one of the two panels used during the preheating.

4. *Panel Construction*.—The test brick shall be laid up so as to form a panel not less than 18 in. square, so that a 9- by $21\frac{1}{2}$ -in. surface of each brick will be exposed to the heat-treatment. Each test brick shall be labeled with ceramic paint on the face opposite that to be tested and then weighed to the nearest 0.05 lb. There shall be placed about the panel test specimen a suitable grade of refractory dummy brick, in the manner shown in Fig. 266a. The dummy brick shall extend $\frac{1}{2}$ in. beyond the surface of the test panel. All brick in the test panel shall be laid up with refractory kaolin unless otherwise specified. The joints shall not be thicker than $\frac{1}{16}$ in. The insulation shall consist of a material suitable for service at 1300°C . and of a specified insulating value.

5. *Preheating Test Panels*.—The prepared test panels shall be placed in position on either side of the preheating furnace. When only one lot

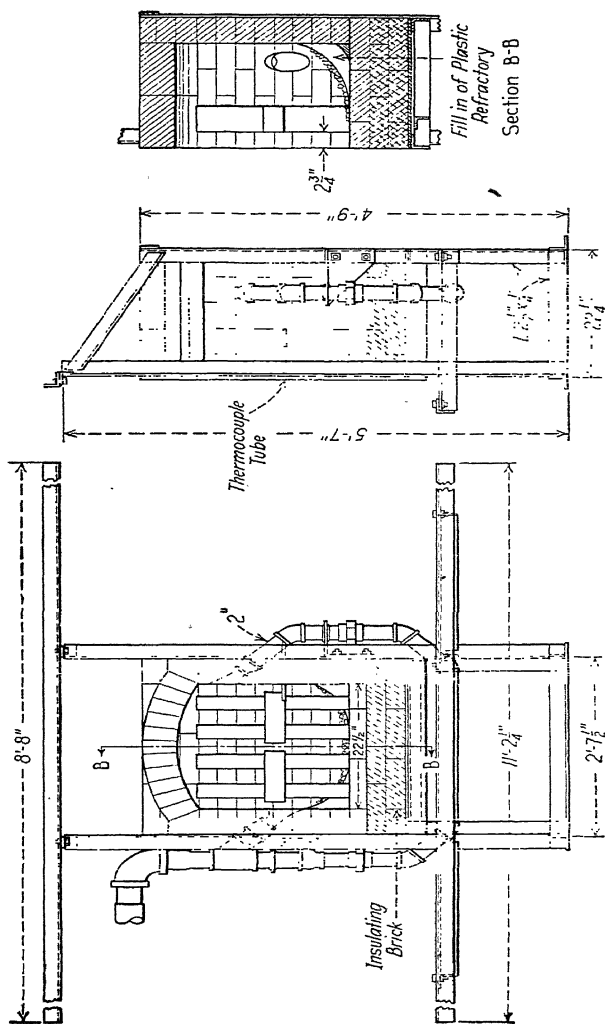


Fig. 265c. Furnace of the spalling equipment.

of brick is to be tested, a dummy panel should be used. The joint between the ends of the panel dummy brick and the preheating furnace shall be sealed with plastic kaolin. During the heating of the panels, the surface of the test brick opposite that being heated shall be insulated in the specified manner so as to maintain a suitable temperature gradient in the test brick. The furnace is to be operated so that the temperature specified for preheating shall be reached in not less than 5 hr. nor more than 8 hr. and maintained 24 hr. The permissible variation in tem-

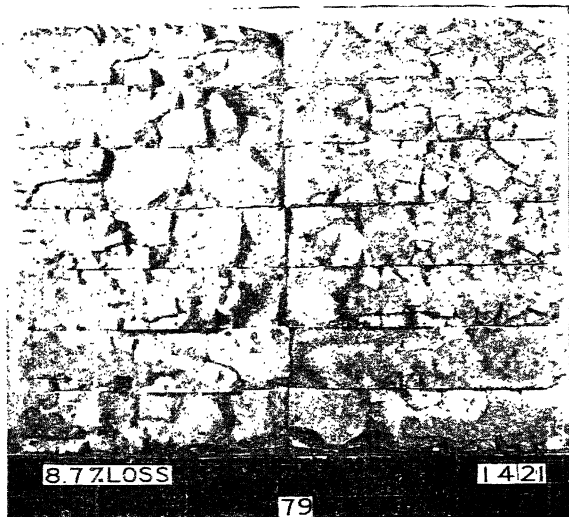


FIG. 266d.—A typical panel after the spalling test. (Courtesy of the American Refractories Institute.)

perature may be $\pm 20^{\circ}\text{F}$ or $\pm 10^{\circ}\text{C}$., but the average of the temperature during the run shall be that specified. After completing the preheating, the test panel shall be left in position for not less than 8 hr. before being removed. As a result of this heat-treatment, any tendency toward fusion, vitrification, swelling, or shrinkage will be evident and any development of structural spalling will be apparent. A record shall be made of the condition of the brick, indicating the extent of the fusion, vitrification, swelling, or shrinkage. If shrinkage takes place, a record shall be made of its nature, *i.e.*, whether this occurs as a shrinkage of each brick as a unit or as the development of cracks on the surface of each brick. The surface of the test panels may be photographed.

6. Spalling.—The panels shall then be subjected to thermal spalling by heating them in a specified time to a specified temperature and

rapidly cooling by means of a prescribed blast. The panels shall be placed in position in front of the spalling furnace in the manner shown in Fig. 266c. The temperature of the spalling furnace shall be raised within 3 hr. to the specified temperature. During the heating period, the panels shall be alternately placed in position in front of the furnace so that each may be heated to about the same temperature. The position of the panels shall be changed at temperatures of 400, 200 and 100°C. below the final furnace temperature. During this period, the panels shall not be cooled by means of the cooling blast. After the final temperature of spalling is obtained, the panels shall be held in position for a specified time and then shifted so as to expose the heated panel for cooling. After each panel has been subjected to the required number of cycles, the furnace shall be allowed to cool, but the cooling procedure for the panels shall be conducted so that each panel receives two additional periods.

7. Dismantling the Panels.—When the panels have cooled sufficiently so that the brick can be handled, the test panel shall be carefully dismantled. The test brick shall be reweighed to the closest 0.05 lb., and the loss in weight recorded as percentage of the original weight.

8. Report.—The report may include a photograph of the panel after preheating and shall include comments as to its condition. The average spalling loss for the whole panel shall be given, as well as a photograph of the spalled brick arranged in the manner shown in Fig. 266d.

STANDARD METHOD OF PANEL TEST FOR RESISTANCE TO THERMAL AND STRUCTURAL SPALLING OF HIGH HEAT DUTY FIRECLAY BRICK

A.S.T.M. Designation: C 107-42¹

ADOPTED, 1936; REVISED, 1940, 1942

This Standard of the American Society for Testing Materials is issued under the fixed designation C 107; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

1. Scope.—This method of test covers the procedure for determining the resistance of fireclay brick used for stationary boilers, malleable-iron furnace bungs, and incinerator furnaces to the separate and combined effects of structural and thermal spalling. This method makes use of the general requirements and procedure prescribed in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (A.S.T.M.) Designation: C 38) of the American Society for Testing Materials and supplements that method by giving

¹ A.S.T.M. Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

the detailed requirements of the procedure to be followed in testing refractories for use in stationary boilers, malleable-iron furnace bungs, and incinerator furnaces.

2. Apparatus and Test Specimens.—The apparatus and test specimens shall be in general as described in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (A.S.T.M. Designation: C 38) of the American Society for Testing Materials.

3. Procedure.—The procedure shall be in general as outlined in the Method C 38, supplemented by the procedure for preheating and spalling as prescribed in the following Sections 4 and 5.

4. Preheating Test Panels.

a. The test brick shall be laid up with kaolin having a pyrometric cone equivalent not below cone No. 34.

b. The test panels and dummy brick shall be insulated with group 26 insulating fire brick weighing 46 ± 2 lb. per cu. ft.

c. The temperature of the panel faces shall be maintained so as to average 2910°F. (1600°C.) by means of a gas-fired furnace for a period of 24 hr.

d. The furnace gas pressure during the 24-hr. preheating period shall be within the limits of 0.4 to 0.5 in. of water for gas-fired furnaces.

5. Spalling.—*a.* The panel insulation shall be removed.

b. The gas-fired furnace shall be operated so as to obtain a temperature of 2550°F. (1400°C.) before the panels are cooled by means of the blast.

c. The period for heating shall be 10 min. and for cooling 10 min., making a 20-min. cycle.

d. The cooling shall be accomplished by means of an air-water mist blast, which shall be delivered through a vertical manifold with an opening measuring $3\frac{1}{2}$ by 24 in. as shown in the Method C 38. Air shall be delivered through each cooling unit at the rate of 1,400 cu. ft. per min. The water used in the four spray units shall be filtered and measured by means of a meter. The spray nozzles shall be regulated so as to deliver water at the rate of $2\frac{1}{2}$ gal. during the first 8 min. of the cycle. No water shall be used during the last 2 min. The cooling units shall be operated with a reciprocating motion so as to pass back and forth across the surface of the entire panel, including the dummy guard brick, 125 times in 10 min.

e. The spalling treatment shall consist of 12 cycles, after which the furnace shall be shut off and the panels given 2 additional cooling cycles without the water mist.

f. After carefully dismantling the panel, the kaolin shall be scraped off with a trowel, removing such pieces of the brick that separate easily.

No attempt shall be made to separate pieces that might be removed by prying or tapping.

STANDARD METHOD OF PANEL TEST FOR RESISTANCE TO THERMAL AND STRUCTURAL SPALLING OF SUPER DUTY FIRECLAY BRICK

A.S.T.M. Designation: C 122-42

ADOPTED, 1937; REVISED, 1940, 1942

This Standard of the American Society for Testing Materials is issued under the fixed designation C 122; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

1. Scope.—This method of test covers the procedure for determining the resistance of super duty fireclay brick to the separate and combined effects of structural and thermal spalling. This method makes use of the general requirements and procedure prescribed in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (A.S.T.M. Designation: C 38) of the American Society for Testing Materials, and supplements that method by giving the detailed requirements of the procedure to be followed in testing super duty fireclay brick.

2. Apparatus and Test Specimens.—The apparatus and test specimens shall be in general as described in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (A.S.T.M. Designation: C 38) of the American Society for Testing Materials.

3. Procedure.—The procedure shall be in general as outlined in Method C 38, supplemented by the procedure for preheating and spalling as prescribed in the following Sections 4 and 5.

4. Preheating Test Panels.

a. The test brick shall be laid up with kaolin having a pyrometric cone equivalent not below cone No. 34.

b. The test panels and dummy brick shall be insulated with group 26 insulating fire brick weighing 46 ± 2 lb. per cu. ft.

c. The temperature of the panel faces shall be maintained so as to average 3000°F. (1650°C.) by means of a gas-fired furnace for a period of 24 hr.

d. The furnace gas pressure during the 24-hr. preheating period shall be within the limits of 0.4 to 0.5 in. of water for gas-fired furnaces.

5. Spalling.

a. The panel insulation shall be removed.

b. The gas-fired furnace shall be operated so as to obtain a temperature of 2550°F. (1400°C.) before the panels are cooled by means of the blast.

c. The period for heating shall be 10 min. and for cooling 10 min., making a 20-min. cycle.

d. The cooling shall be accomplished by means of an air-water mist blast, which shall be delivered through a vertical manifold with an opening measuring 3½ by 24 in. as shown in the Method C 38. Air shall be delivered through each cooling unit at the rate of 1,400 cu. ft. per min. The water used in the four spray units shall be filtered and measured by means of a meter. The spray nozzles shall be regulated so as to deliver water at the rate of 2½ gal. during the first 8 min. of the cycle. No water shall be used during the last 2 min. The cooling units shall be operated with a reciprocating motion so as to pass back and forth across the surface of the entire panel, including the dummy guard brick, 125 times in 10 min.

e. The spalling treatment shall consist of 12 cycles, after which the furnace shall be shut off and the panels given 2 additional cooling cycles without the water mist.

f. After carefully dismantling the panel, the kaolin shall be scraped off with a trowel, removing such pieces of the brick that separate easily. No attempt shall be made to separate pieces that might be removed by prying or tapping.

In using the A.S.T.M. panel test for spalling, the following losses are generally used as limits.

Conditions	Average Weight Loss, Per Cent
Average spalling.....	15
Moderately severe.....	10
Severe (malleable furnace bungs)...	5-7.5
Extremely severe (super duty class)...	4

The A.S.T.M. panel spalling test equipment has been installed in a number of laboratories and, in spite of the considerable cost of operation and large floor space required, has been well worth while when reliable spalling results are required. This test is valuable to the producer of refractories for a control test of his product and for the development of improved refractories. It also is of aid to the consumer in assuring that the standard of quality of the refractories purchased is adhered to. Those who do not have enough testing to justify the cost of this equipment may have their product tested at a commercial testing laboratory.

The U.S. Navy simulative service furnace, as described in Chap. XVI, can be used for a spalling test with results agreeing well with those obtained in service.

7. Spalling Characteristics of Various Bricks.—In Table 66 are given the spalling resistance of a number of fireclay brick as measured by the A.S.T.M. panel spalling test.

Silica brick are not at all resistant to spalling in the low-temperature range; but once they are above the inversion temperature, they are very resistant to wide changes in temperature because of the flatness of the expansion curve in this region. This is the reason that they give such good service in regenerative furnaces.

Chrome and magnesite brick, because of their rather high coefficient of thermal expansion, are not so resistant to spalling as fireclay brick, but great improvements have been made in the last few years in providing a more flexible structure⁽²⁶⁾ and thus increased resistance.

Silicon carbide brick have an excellent resistance to spalling.

TABLE 66.—SPALLING RESISTANCE OF FIRECLAY BRICK BY THE A.S.T.M. PANEL SPALLING TEST*

(Courtesy of the American Refractories Institute)

Method of manufacture	Loss in panel spalling test, per cent	Porosity, per cent
Hand-made.	12.8	17.8
	8.0	25.0
	6.3	24.0
	21.0	22.4
	25.0	15.7
Stiff-mud.	28.0	13.7
	20.5	20.1
	2.5	24.4
	0.5	30.0
	14.8	20.9
Dry-press.	5.5	16.7
	13.0	17.5
	2.0	23.0
	1.0	14.0

* These panels were preheated to 1600°C. according to specifications C-107.

8. **Effect of the Brick Structure on Spalling.**—The structure of the brick and the method of manufacture have a considerable

influence on spalling. Data given below illustrate the effect of various factors. These data are for one particular clay and will not be exactly the same for others, but the trend should be general.

Effect of Grog Size.—A number of bricks were made up with various sizes of grog, other conditions being the same. The spalling resistance for each grog size is given in Table 67 below. The spalling resistance increases steadily with the grog size for a given burning temperature. These results were obtained on single bricks, and somewhat different values might be obtained by panel spalling methods.

TABLE 67.—EFFECT OF GROG SIZE ON SPALLING RESISTANCE

Burned at	1649°C. (3000°F.)	1677°C. (3051°F.)	1704°C. (3099°F.)
2 mesh.....	20 cycles	12 cycles	5 cycles
3½ mesh.....	11 cycles	6 cycles	3 cycles
4 mesh.....	6 cycles	3 cycles	1 cycle
20 mesh.....	1 cycle	1 cycle	1 cycle

Effect of Amount of Grog.—In Fig. 267 is plotted a curve of spalling resistance against percentage of grog. It is interesting to note that the maximum spalling resistance occurs at 40 per cent

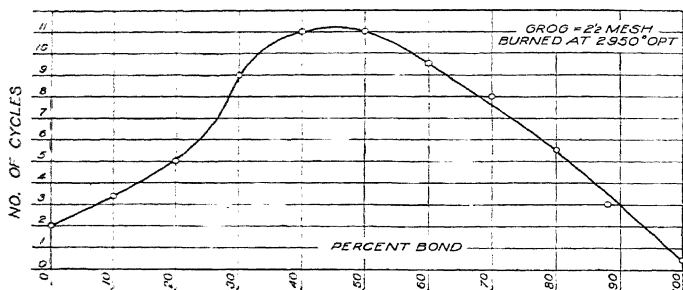


FIG. 267.—The influence of the amount of bond on spalling resistance.

of bond, or at the condition where the pores are just filled up. Above or below this point, the spalling resistance falls off rapidly, probably owing to loss of flexibility.

Effect of Burning Temperature.—Figure 268 shows a curve of spalling resistance plotted against burning temperature. There is a minimum value at 1620°C. (2950°F.) and a maximum at

1650°C. (3000°F.). This type of curve has been observed a number of times for this particular brick, but it may not apply to all others. The minimum point is probably due to the decreasing flexibility of the structure with increased temperature. Beyond 1600°C. (2950°F.), the free silica is dissolved and the coefficient

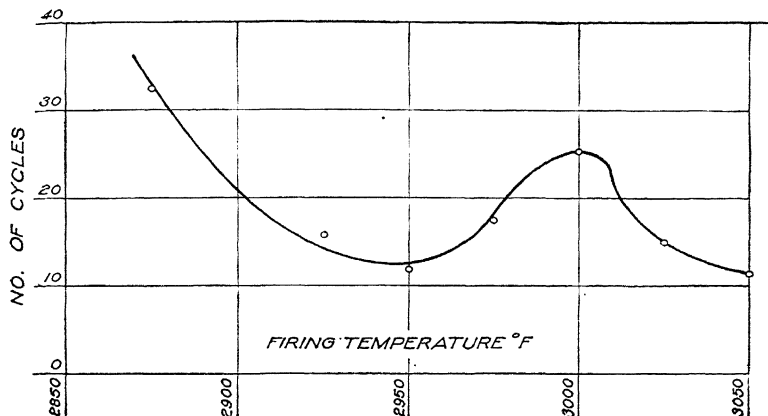


FIG. 268.—Influence of burning temperature on spalling resistance.

of thermal expansion is lowered, which increases the spalling resistance up to 1635°C. (3000°F.). After this, the structure gets more rigid and the spalling resistance falls off. In general, it may be said that increasing the burning temperature decreases the resistance to spalling. This is shown in Table 68, where the

TABLE 68.—EFFECT OF PREHEATING ON SPALLING RESISTANCE

Brick	As burned, cycles	Preheated to 1670°C. (3038°F.) cycles
Missouri.....	45	4
Missouri (diaspore).....	29	13
	12	1
	18	4
Pennsylvania.....	15	1
	22	2
	11	1
	4	1
Kaolin.....	12	12

spalling resistance is given for a number of bricks before and after preheating. Again it is probable that the hard-burned bricks would have shown up comparatively better if the spalling had been made with the panel test.

Characteristics of a Good Spall-resisting Brick.—We usually have a specified material from which to make a brick. With this material, it is impossible to alter the diffusivity appreciably, and only small changes can be made in the coefficient of thermal expansion. Therefore, if we desire to make the best spall-resistant brick from

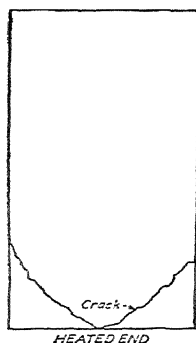


FIG. 269.—A type of spalling fracture often occurring in service. (*J. Am. Ceram. Soc.*)

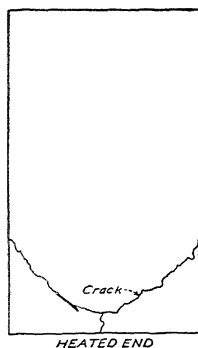


FIG. 270.—Tension crack in end of a brick due to spalling. (*J. Am. Ceram. Soc.*)

a given material, we must do two things: (1) make a structure having the greatest possible flexibility and (2) eliminate all possible flaws and laminations.

Flexibility can best be obtained by using a large size of grog, a high degree of porosity, and a low degree of vitrification. These characteristics cannot be obtained to a high degree without sacrificing others of considerable importance. For example, bricks could easily be made to withstand 50 cycles in the air-spalling test; yet they would be mechanically weak and would probably have a high residual shrinkage. It has often been noticed that when a series of bricks are tested for spalling, there will be a great variation between the best and the worst out of

the same lot. Where it is known that these bricks were made by identically the same process and that they all were burned at the same temperature, we can conclude only that the difference in spalling resistance is due to some lack of homogeneity in the structure of the brick. It is impossible to state definitely that any one method of making bricks gives the best or the worst spalling results, although it is generally found that repressed

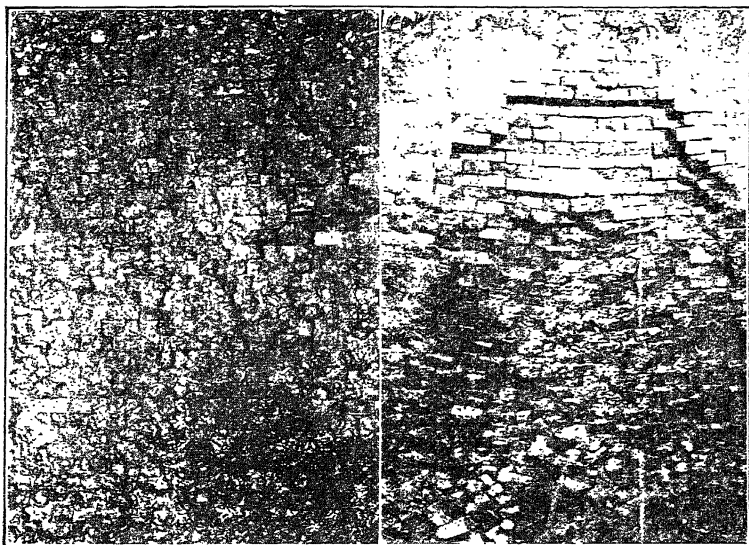


FIG. 271.

FIG. 272.

FIGS. 271 and 272.—Boiler furnace wall showing spalling under oil-fired conditions. (*Stone and Webster Company.*)

bricks, when properly tempered, give greater uniformity in the spalling test. We are greatly in need of some simple test to determine which bricks in a given lot will give a poor resistance to spalling. Some investigations have been made to test each brick by noting the sound emitted when struck with a hammer; but as yet, no very definite results have been obtained along this line.

9. Spalling Fractures in Service.—The types of spalling fracture in service walls are quite varied. Perhaps the most typical is that shown in Fig. 269, which consists of two shear cracks com-

ing together at the center of the brick. There is often a small tension crack in the end of the brick, as shown in Fig. 270. The fracture corresponds well with the determined stresses for this condition. This type of failure is not often serious, because the fragments are so large that they stay in place. In other cases, the wall is pretty well shattered, as shown in Figs. 271 and 272.

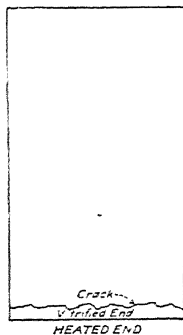


FIG. 273.—Separation of a thin layer due to vitrification. (*J. Am. Ceram. Soc.*)

Another type of spalling failure is the separation of a thin layer of material from the face of the brick, as shown in Fig. 273. This usually occurs with bricks of low vitrifying points or with slagged surfaces, and the fracture runs between the vitrified material and the body of the brick. Often layer after layer will peel off, giving a considerable length of service before the wall becomes too thin.

Exposed corners in a furnace are quite subject to spalling and should be avoided in design where possible. This type of failure by shear is shown in Fig. 274.

Spalling in a wall is greatly augmented by compression loads due to expansion. Expansion joints should be left at least every 15 ft. and should amount to $1\frac{1}{2}$ to 1 in. Another method is to place a slip of thin cardboard between bricks in each vertical joint (or thicker pieces in alternate joints). These will burn out and allow each brick to expand freely, and yet there will be no general movement of the wall. Thin pieces of steel, which are pulled out as the wall progresses, have sometimes been used instead of the cardboard.

In the case of arches, there is often a pinching off of the tips due to temperature strains. Care, however, should be taken to see that there is clearance between the inner ends when temperature or load conditions are severe.

Failure due to heating wet brickwork rapidly is sometimes considered spalling. The remedy is obvious. Mechanical breakage when slicing off slag deposits is also classed as spalling by some people. The brick manufacturer can do little to help this failure

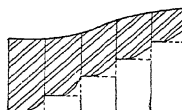


FIG. 274.—Spalling of exposed corners of a furnace.

except to supply the hardest bricks that will stand the temperature changes.

There has perhaps been too great a tendency for manufacturers and users of refractories to specify brick with a good spall-resisting quality, as judged by the laboratory test. Many cases have come up where a hard, dense brick has stood up in service far better than one with a good spall-test record. This is probably due not to any fault in the test but to conditions of mechanical loads in service not encountered in the laboratory.

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CHAPTER XV

THE REACTION BETWEEN REFRACTORIES AND SLAGS OR GLASSES

1. Chemical Effect of Slag Action.—In general, slag action can be divided into chemical effects and physical effects, the first of which will now be considered.

Equilibrium Conditions.—It is very important to make a distinction between equilibrium conditions and the rate of reaction. For example, if an intimate mixture of magnesia and silica is maintained at a definite temperature, it will, after a certain length of time, be converted into magnesium silicate with a relatively low melting point. When the conversion is as complete as the proportion of the substances permits, equilibrium is attained and no further change will occur at that temperature. If the temperature is low, this reaction will progress with extreme slowness; but on the other hand, if the temperature is high, the reaction will take place rapidly; however, in each case, a state of equilibrium will be reached. It will first be advisable to investigate the equilibrium conditions for the combinations of various slags and refractories; for if the equilibrium conditions produce no material melting at a temperature lower than that at which the refractory is maintained, there can be no serious slag reaction. In such a case, the rate of reaction would not concern us. Usually, however, the slag or the material produced by the reaction of the slag with the refractory melts at a lower temperature than that maintained in the furnace.

Owing to the great complexity of the materials entering into slag and glass reactions, we do not have very complete information on the equilibrium diagrams concerned in these reactions. More data of this type are greatly needed. However, it can be stated in general that (the slag reaction depends upon the formation of a low-melting compound or mixture.)

Composition of Slags and Glasses.—Table 69 shows typical analyses of commercial slags and glasses. In general, each one

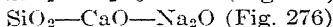
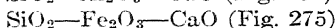
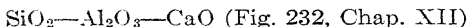
TABLE 69.—ANALYSES OF TYPICAL SLAGS AND GLASSES

	Portland cement clinker	Lead blast furnace	Copper reverberatory	Coal ash, Ind.	Coal ash, Ill.	Acid, open hearth	Basic, open hearth	Blast furnace	Heating furnace	Window glass	Opal glass	Borosilicate glass	Fuel oil
SiO ₂	21.9	32.6	47.4	42	43	50.1	23.3	36.8	17.0	72.10	65.8	80.6	44.0
Al ₂ O ₃	5.6	3.1	29.0	15	17	3.0	0.3	11.7	3.9	0.80	6.6	2.0	1.3
Fe ₂ O ₃	4.6	30.4*	34.5*	33	27	30.3*	26.6*	3.4*	75.3	0.08		0.2	
TiO ₂					1	1.5	1.0	0.5	0.7				27.7
CaO	65.8	19.1	9.4	3	7	2.3	38.0	43.4	0.8	9.10	10.1	0.2	22.5
MgO	1.4	1.8	1.4	Trace	1	0.9	7.0	2.5	0.1	1.30		0.3	
MnO		0.9	0.4			11.7	4.2	0.9	1.9				
Na ₂ O						Trace	0.1	0.6	0.1	16.20	3.8	3.8	3.3
K ₂ O				7	4						9.6	0.6	1.0
V ₂ O ₅													
ZnO		8.3	1.5										
CuO		0.2	0.5										
PbO		1.2	0.3										
SO ₂	0.2									0.5			
As ₂ O ₃										Trace		0.7	
F											5.3		

* Chiefly FeO.

has so many elements present that it is difficult to tie them in with any simple system; and when the elements in the refractory are added, the complexity is still further increased.

Equilibrium Diagrams.—It will be seen from Table 69 that the systems particularly applicable to slag-refractory reactions are



It should not be forgotten that small amounts of some other materials such as PbO or F may greatly influence the slag action.

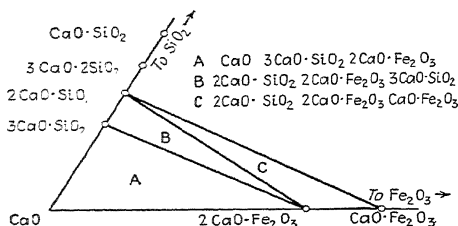


FIG. 275.—Composition triangles in system CaO-SiO₂-Fe₂O₃. (W. C. Hansen and R. H. Bogue, *J. Am. Chem. Soc.*)

Rate of Reactions.—The second factor in slag reactions is the rate at which reactions occur. Suppose that a refractory is washed by a slag capable of combining with the refractory to form a low-melting compound. If the reaction occurs rapidly, these low-melting compounds will be formed in considerable quantities and will run off the face of the wall, thereby exposing fresh surfaces for the attack of the slag; therefore the slag resistance of the refractory will be poor. On the other hand, let us suppose that the same low-melting-point compounds are formed but that the rate of reaction is slow. Then the compounds will be formed in small quantities, and the resistance of the refractory to the slag may be good. This is the reason why the prevalent idea that basic refractories must be used with basic slags and acid refractories with acid slags is not necessarily true. Although the acidic and basic qualities determine the formation products, they do not necessarily determine the rates of reaction. For example, magnesite will stand up well under the action of certain highly

siliceous slags, and silica bricks are known to give good service in lime kilns under highly basic conditions. .

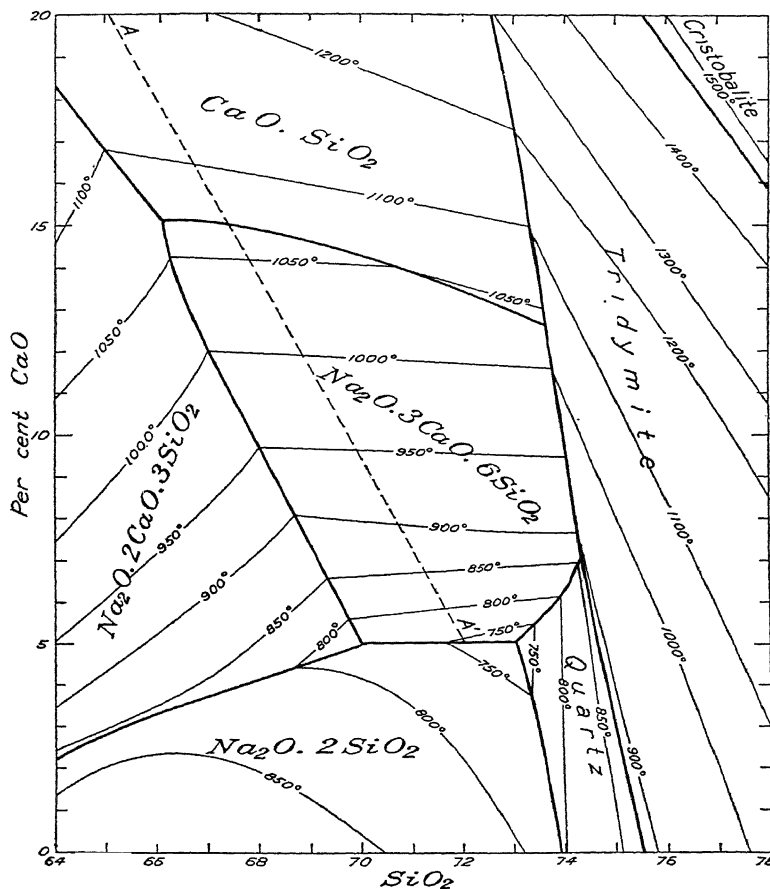


FIG. 276.—Part of the ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$. (Hall and Insley.)

The rate of reaction is greatly influenced by the temperature. In many instances, an increase of 10°C . (18°F .) will double the rate of reaction. This is the principal reason why certain refrac-

tories will resist slag very well at the usual working temperatures but will be rapidly eaten away if the furnace temperature is increased by 50°C. (90°F.). Unfortunately, practically no information is available, owing mainly to the experimental difficulties, on the rate of reaction of the materials in which we are interested at high temperatures. However, the reaction rate may be approximately expressed by the following equation of Arrhenius:

$$\log \frac{K_{t_2}}{K_{t_1}} = A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where K_{t_1} = the reaction velocity at temperature T_1 , deg. abs.

K_{t_2} = the reaction velocity at temperature T_2 , deg. abs.

A = a constant of the reaction

The value of A varies but is in the neighborhood of 10,000 for clays and fluxes.

2. Physical Effects of Slag Action. *Velocity of Flow.*—As the rate of reaction is dependent upon the concentration of the slagging material on the surface of the refractory, it is evident that the more rapid the movement of the liquid slag over the refractory surface the more rapidly the fresh slag will be presented to the surface. It is well known that a liquid may flow in two ways. The first is a streamline flow, where the direction of the flow is parallel to the surface over which it is flowing; and the second, a turbulent flow, where the particles of the liquid are undergoing motion in various directions. The transition from streamline flow to turbulent flow depends upon the size, velocity, and viscosity of the melt. It is evident that turbulent flow is much more effective in bringing fresh slag to the surface than is streamline flow; so it is desirable to keep the velocity of flow low and the viscosity high. As the viscosity is dependent upon the temperature, we have another reason why high temperatures promote more rapid slag reaction. It may be said that in general, all slag flows are of the streamline type where the slag is flowing in thin layers over the refractory but, in the cases where the slag is in large quantities, as in glass tanks, the flow may be of the turbulent type for the more fluid glasses.

Diffusion in the Melt.—Another physical effect that has an influence on the rate of slag attack is diffusion through the molten

slag. Very little is known about the rate of diffusion of substances at high temperatures, but it is possible that this effect is quite important in bringing the reacting substances together. Bowen has shown that the rate of diffusion of silicates of the type of diopside in each other at 1500°C. (2732°F.) is comparatively rapid. The rate of diffusion is proportional to the viscosity and therefore depends largely upon the temperature of the melt.

Gas Diffusion through Melt.—Sosman has suggested that another type of diffusion may have considerable influence on slag action. This is the phenomenon of the diffusion of gases through the melt. It has been shown that hydrogen and helium will pass through vitreous quartz glass at high temperatures so rapidly as to assume the character of an actual flow of gas.

Slag Penetration.—In the previous discussion, we have considered the reaction occurring between the surface of the refractory and the molten slag. If the refractory is a dense material, this surface will be smooth; but, on the other hand, if the refractory is porous, the surface may be considerably increased owing to penetration of the slag into the pores. A number of refractories are made from a hard grog and a softer bond, in which case the slag will react with the bond more rapidly than with the grog particles and will allow the latter to project from the surface. It often happens that these grog particles are carried away in the melt before they have become dissolved. This has been noticed in glass melts and, of course, is harmful to the glass. Other types of refractories, even though composed of homogeneous material, will allow the rapid penetration of the slag into the interior.

Recent results on glass-tank blocks have shown that a high porosity may not cause susceptibility to slag action, provided the pores are all below a size that will allow the slag to be drawn in by capillary forces. On the other hand, flaws, laminations, or cracks are very harmful and allow rapid slag penetration.

Wetting of the Surface by Slag.—There is another side to slag reactions which has not, it is believed, been generally discussed, *i.e.*, the wetting of the refractory surface by the molten slag. It has been noticed that when certain slags are applied to some refractories, they will melt on the surface and form in drops without wetting the surface. A refractory, under such conditions, is practically unaffected by the slag. This condition is just the

opposite of many other cases, where the slag is drawn by capillary attraction deep into the pores. It seems quite reasonable to believe that the wetting by the molten slag in contact with the refractory may have a very important influence on the slag resistance of that refractory, and data on the surface tension under these conditions would be of considerable value.

3. Laboratory Slag Tests.—Of all laboratory tests for refractories, the least satisfactory is the slag test, for it is difficult in a reasonably short time to evaluate the resistance of a refractory.

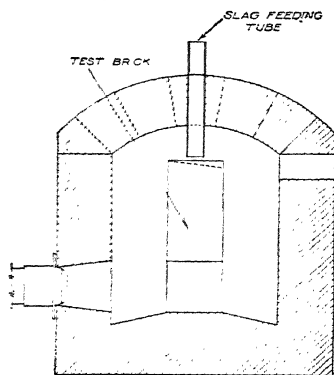


FIG. 277.—Slag-test burner.

To accelerate the action by higher temperatures or by a greater flow of slag may materially alter the conditions of reaction.

Early Methods of Test.—Some of the proposed methods of slag testing consisted in measuring the penetration of slag into the refractory, the fusion point of powdered slag and refractory when mixed together, and the petrographic study of mixtures of slag and refractory after definite heat-treatments.

These methods measure some factors of slag reaction but not by any means all of them.

Refractory in Slag Baths.—A number of experimenters have measured the resistance of a refractory to slags by suspending them in a bath of molten slag, with motion to bring new slag to the surface. The test of Endell, Fehling, and Kley⁽¹⁰⁾ used this method with considerable success.

Running Slag Test.—Another method suggested by Prof. G. B. Wilkes consists of heating a single brick or a column of bricks to a uniform temperature and regularly dropping powdered slag on top, allowing it to run down the face in a groove, as shown in Fig. 277. The depth to which this groove has been cut at the end of the test gives a very good indication of the slag resistance of the brick, because the test is carried on under conditions closely approximating those of service. Although this test gives excellent relative values, it is not a quantitative test and does not

maintain a proper temperature gradient from the slag surface to the other face: ✓Hartmann⁽¹⁸⁾ used a similar method with a small specimen in an electric furnace.

Spray Slag Tests.—Perhaps one of the most satisfactory tests consists in spraying powdered slag against the heated refractory. ✓A number of experimenters have used this method, but the most

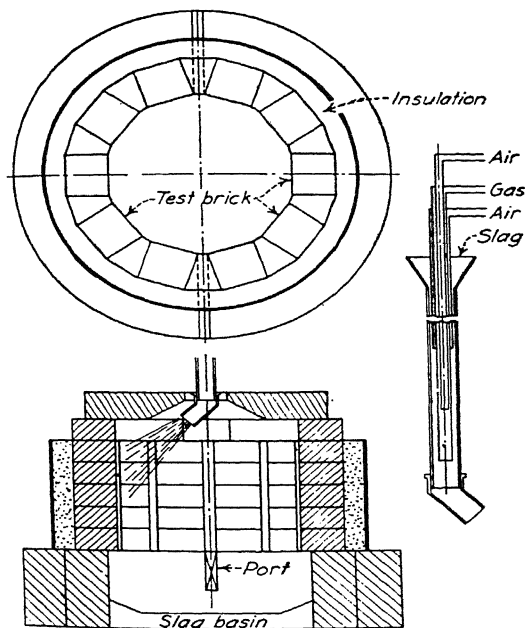


FIG. 278.—Slag-test furnace and burner.

practical furnace is that used by Hursh^(22,31) as shown in Fig. 278. Here the powdered slag is fed through a revolving burner impinging on the test bricks set on the inside of the cylindrical furnace. Thus, all the bricks get the same treatment and the temperature gradient through the bricks is similar to that found in service. If the test is run for several days, truly quantitative values can be obtained. ✓

Tanks for Testing Glass Refractories.—The only really satisfactory way to test glass-tank blocks is to use them in a small tank that is fed and drawn at regular intervals. A satisfactory tank for this purpose, shown in Fig. 279, is about the minimum size that can be used successfully. A two-weeks' run will give a fair indication of the resistance to the glass, but a longer run is sometimes desirable.

4. The Slag Resistance of Refractories.—There are so few really quantitative data on the resistance of refractories to slags that it would seem impossible at the present time to give a table

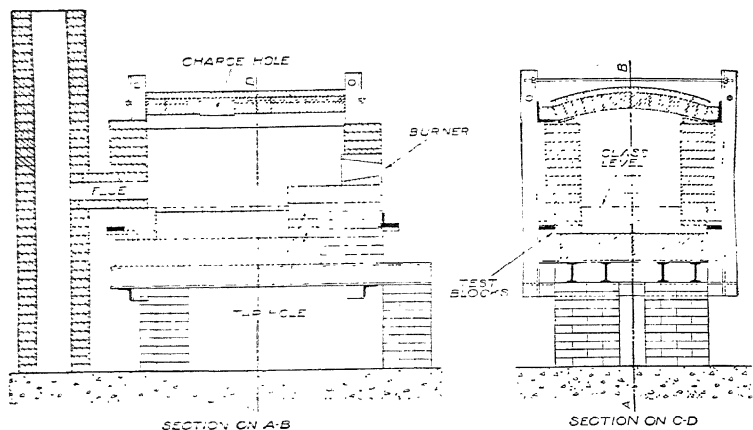


FIG. 279.—Small tank with a 3 × 5 ft. melting chamber. (Courtesy of the Babcock and Wilcox Company.)

of values that would mean very much. However, from our experience in the use of refractories, certain conclusions can be drawn which will be discussed in Part IV.

5. The Products Formed in Slag Reactions. *Fireclay Refractories and Coal-ash Slag.*—The microscopic examination of the boundary layer between the slag and refractory indicates several definite zones that are generally present in all slagging of this nature. A study of these conditions has been made by McDowell and Lee,⁽¹⁰¹⁾ McVay and Hursh,⁽¹⁰²⁾ and others. On the furnace side, there is a layer of slag that, at high temperatures, may be very thin, perhaps 1 mm., but, at lower temperatures, may build

up to a coating of several centimeters. This layer of slag usually contains anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, associated with iron oxide which may be in any of several forms, depending upon the atmosphere of the furnace. Mullite crystals are also present, but they usually contain iron oxide in solid solution.

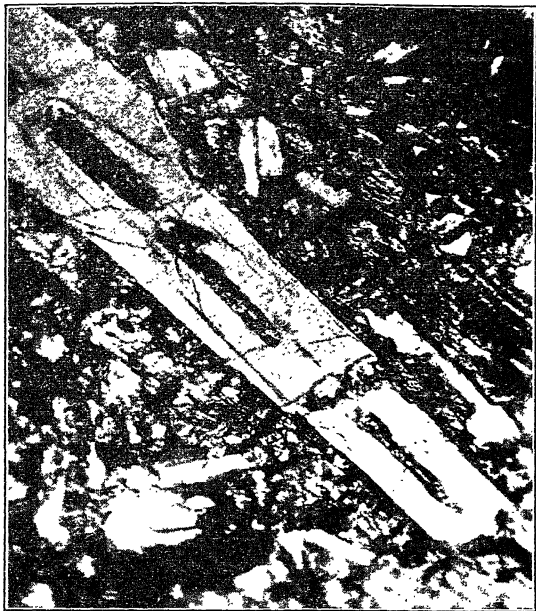


FIG. 280.—Thin section of Illinois coal-ash slag which was slowly cooled. The large crystal shown is feldspar; 250 diameters, with crossed Nicol prisms and a gypsum plate.

The next zone, which is the transition zone between the slag and refractory, contains mainly large and well-developed mullite crystals. As in nearly every case of slagging between firebrick and slag or glass, the development of mullite crystals is accelerated in this intermediate zone.

The next zone is in the body of the refractory itself and generally shows some penetration of the slag into the pores of the brick and, in many cases, the initial solution of particles of the refractory.

In the case of a firebrick crown that is swept by powdered slag, stalactites form and drip off the roof. Here the composition may be somewhat different from the slag on the side walls because more time is available for equilibrium to be established before the slag runs off. An examination of the stalactites shows magnetite and anorthite crystals well developed; and in a few instances, mullite crystals have been observed.



FIG. 281.—A thin section of a sample of opal glass which was near the refractory, showing dendritic crystals of cristobalite; 1,260 diameters, with ordinary transmitted light.

High-alumina Refractories and Coal-ash Slag.—Refractories containing a high percentage of mullite, which have been made from kyanite and diasporé, show somewhat different characteristics under the action of slag. The first characteristic that will be noticed is that the slag penetrates deeply into the refractory and leaves little on the surface. On the surface of the refractory, which is only lightly covered with slag, mullite crystals pre-

dominate; but as we penetrate farther into the body of the refractory, corundum crystals increase in number until they may be equal in volume to the mullite. The zone of corundum crystals seems to give a weaker structure than the zone of inter-



FIG. 282.—Thin section of opal glass taken at a point very close to the refractory. A large number of dendritic cristobalite crystals and a few corundum crystals are seen. A few unidentified crystals of high index are present in this slide; 80 diameters, with ordinary transmitted light.

locking mullite crystals and may present a zone of weakness that will cause spalling. The formation of the corundum crystals indicates a more rapid solution of the silica than of the other constituents, leaving excess alumina behind.

Siliceous Fireclay Refractories and Soda-lime Glass.—The constituents formed between refractories and glass have been examined by Insley,⁽⁷⁶⁾ Wilson,⁽⁷⁴⁾ and Kai-Ching-Lu.⁽⁸⁹⁾ The hottest zone between the glass and the refractory is generally milky white or brownish and contains cristobalite crystals in glass.

Corundum plates and nephelite crystals are sometimes observed here. The next zone as we approach the refractory is a white layer containing mainly mullite crystals. The refractory itself shows penetration of the glass into the pores, but this is not

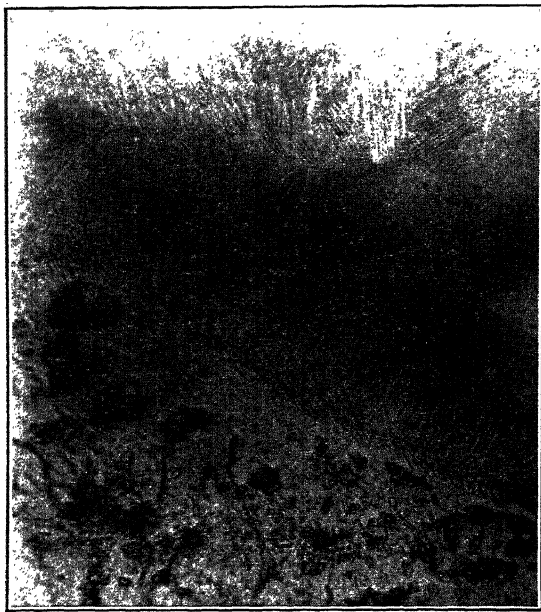


FIG. 283.—Thin section of a glass stone, composed of nephelite which was formed by materials dropping from the crown into the melt. The material at the lower left-hand corner, containing inclusions, is the nephelite. The long slender needles appearing at the edge of the stone are of feldspar; 265 diameters, with crossed Nicol prisms and gypsum plate.

evident at any distance from the surface. Thin sections shown in Figs. 282 to 284 give a clear picture of the crystal formation in glass.

Aluminous Fireclay and Soda-lime Glass.—In this case, the hottest zone is a brown layer containing soda-lime feldspars imbedded in glass. The next layer is white and consists of mullite crystals imbedded in alumina glass with corundum

crystals. The latter are formed from the alumina-saturated glass in this zone.

Silica Brick and Iron.—A careful examination of silica roof brick by Scott⁽¹¹²⁾ shows the following characteristics: The hot



FIG. 284.—Thin section of a stone in a glass melt. This stone was caused by a particle of the refractory being eroded from the side of the glass tank; 500 diameters, with crossed Nicol prism and gypsum plate.

end of the brick is a gray zone of cristobalite crystals and magnetite with, perhaps, a few tridymite crystals at the cooler end; the next cooler zone is black and consists of tridymite, magnetite, and a small percentage of cristobalite; the cooler end of the brick consists of cristobalite, tridymite, and quartz, the last increasing toward the outer end of the brick.

In the hearth, fayalite, Fe_2SiO_4 , and tridymite were found in a brown glass. In the hotter portions, some cristobalite was found and about 20 per cent ferrous oxide was generally present.

Iron silicates do not generally form in large quantities but were present only where the conditions are reducing.

Magnesite and Iron.—In general, magnesite in contact with iron or its oxides gives periclase crystals with iron in solid solution, together with some crystals of magnesioferrite. When lime is present, calcium oxide crystals are formed, sometimes of large size. Crystals of tricalcium silicate have been observed.

Fireclay Refractories and Iron.—The main constituents formed by this reaction are iron silicates and mullite with iron in solid solution.

Alkali Vapors and Refractories.—Alkali vapors or dust are encountered in many industrial furnaces such as glass tanks, boiler furnaces, and blast furnaces. Much work has been done in the last few years on this subject as shown by the references.⁽⁵⁹⁻⁷³⁾ Siliceous-type bricks are not so resistant to alkali vapors as fireclay or aluminous types of brick, owing to the formation of a liquid slag in the first case. According to Hartmann,⁽⁶⁷⁾ magnesite brick are very resistant. Hard firing and low porosity increases the slag resistance of any brick.

Other Slags.—The reaction between refractories and other slags has not been studied to any great extent. Audley⁽¹¹⁷⁾ examined the zinc-fireclay reaction and found the occurrence of a zinc spinel. Turner⁽⁸²⁾ and McSwiney⁽¹¹⁹⁾ have discussed the action of arsenic in glass on refractories, but no definite conclusions have been reached.

We need information on the products formed by copper, lead, and tin when in contact with various refractories. Little is known of the slag reactions with chromite, zirconia, and zircon.

6. Gases and Refractories. *Carbon Monoxide.*—It has been known for a number of years that CO gas at certain temperatures weakens the structure of a firebrick. This effect is particularly noticeable in blast-furnace linings and zinc retorts. A number of investigators have studied the problem, such as Mitra and Silverman,⁽³⁵⁾ Hubbard and Rees,⁽³⁹⁾ and many others listed in the references. In general, it is believed that the starting point of the disintegration is the ferric oxide spots in the refractory. The ferric oxide is reduced to ferrous oxide, which acts as a catalyst to break up the CO to CO₂ and C, forming a deposit that causes the disintegration. This reaction takes place only between 420 to 470°C. (788 to 878°F.). It is believed by Mitra and

Silverman that the magnetic oxide of iron Fe_3O_4 is not susceptible to this action.

A brick to resist CO must be either very low in iron or fired at a temperature high enough to allow the iron to combine with the silica and alumina in the brick.

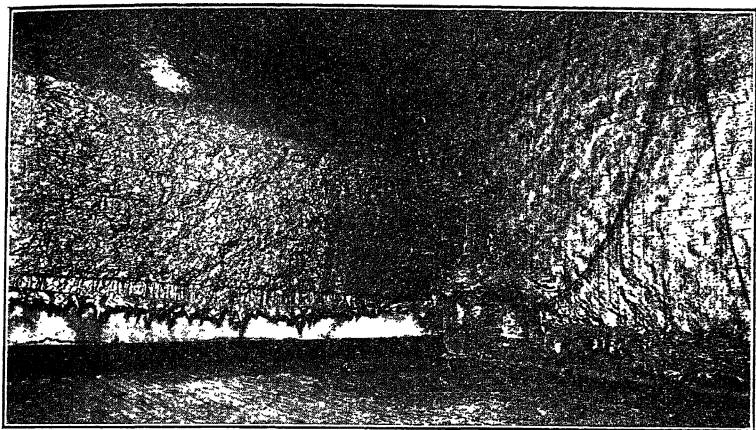


FIG. 285.—Slag erosion of a boiler furnace wall. (Courtesy of Commonwealth Edison Company.)

Hydrocarbon Gases.—A number of investigators have studied the embrittling effect of hydrocarbon gases on fireclay brick in the cracking range of temperature.^(48,50,55,56) The action seems to be similar to that of CO, *i.e.*, a deposition of carbon.

Steam.—In some cases as in water-gas generators, steam has shown a weakening influence on refractories.

Oxygen.—Silicon carbide refractories have a tendency to oxidize slowly. Many efforts have been made to prevent this by glazing the surface as described by Walton⁽⁴⁴⁾ or by removing catalytic agents as described by Hartmann.⁽⁴²⁾

7. Slag Erosion in Service.—The deterioration of refractories by slag is very serious in many types of installation. The action is particularly severe in boiler furnaces where low-grade coal is burned, as the slag formed is a very active flux. In many cases, the only solution to the problem is to use air or water

cooling. Although it might be possible to find a more resistant refractory than fireclay brick, such as magnesite or spinel, the

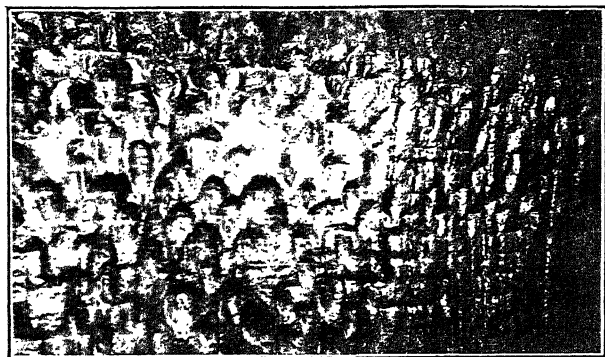


FIG. 286.—Detail of typical slag erosion. (*Courtesy of Commonwealth Edison Company.*)

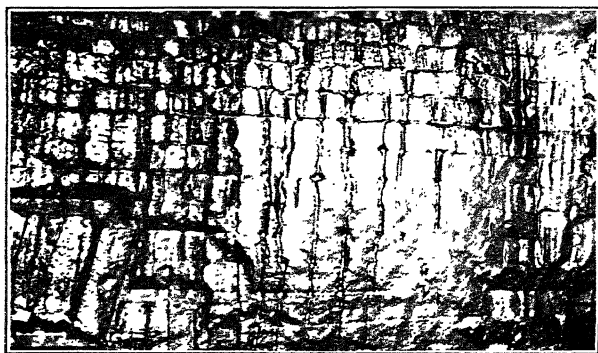


FIG. 287.—Detail of slag erosion. Note the grooving effect. (*Courtesy of Commonwealth Edison Company.*)

rapid heating and cooling of the boiler furnace make the use of these easily spalled materials impossible. Efforts should be made in the design to minimize the flow of slag over the hotter surfaces.

In Figs. 285 to 289 are shown typical boiler-furnace walls that have been eroded by slag. The vertical grooves formed by the

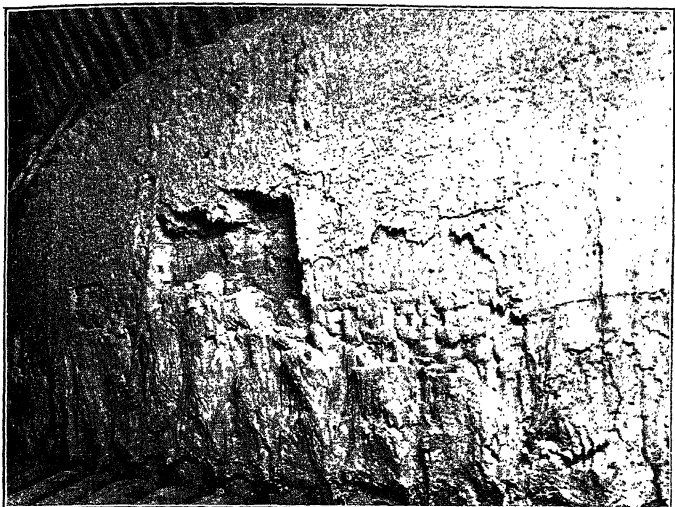


FIG. 288.—A wall coated with a high-fusion-point slag. (*Courtesy of Stone and Webster.*)

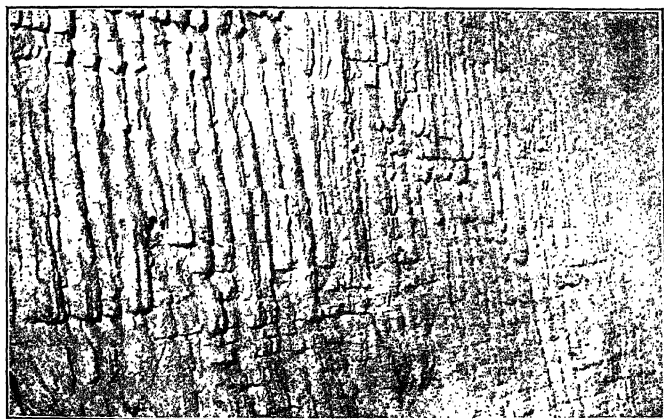


FIG. 289.—Bad grooving by slag on an inclined wall. (*Courtesy of L. E. Hankison.*)

running slag are representative. Where the melting point of the ash is high or the temperature of the furnace is low, the ash will not flow but will form a protective coating on the wall. If this coating does not build up so thickly that it tears off the face of the wall, it serves as a protection to the refractory.



FIG. 290.—Thin section of magnesite refractory which was used in a high-temperature furnace. The dark material in this section is magnesite which contains a considerable amount of iron rendering it fairly opaque. The light-colored crystals which can be seen are the result of the action of the slag on the magnesite; 60 diameters, with crossed Nicol prisms and gypsum plate.

The slag erosion in forging and heating furnaces by the molten mill scale is serious in the bottoms. Magnesite and chrome bottoms have been tried with considerable success under these conditions (Fig. 290).

In steel- and iron-melting operations, the high temperatures and activeness of the slag make the conditions for the refractory very severe. In the open hearth, the continued high temperature allows the use of magnesite or silica bottoms. Where fire-

clay refractories are used, as in the cupola, frequent patchings are necessary. High-alumina refractories seem to show good service in cement kilns (Fig. 291).

Glass tanks are maintained at an even temperature, and rather large blocks of fireclay refractory are generally used. However,

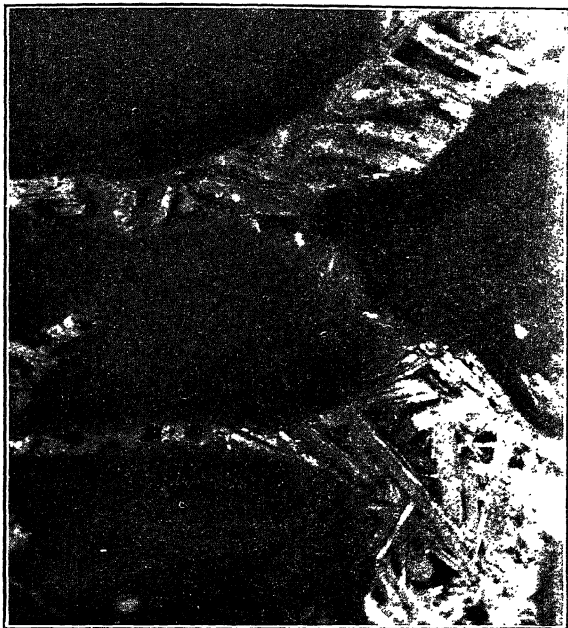


FIG. 291.—Thin section of a refractory used in a rotary cement kiln. The charge has reacted to some extent with the refractory and partially eroded it, with the formation of lime feldspar. These are the light-colored crystals which appear between the grains; 250 diameters, with crossed Nicol prisms and gypsum plate.

the blocks are eaten away fairly rapidly at the metal line. The action of some glasses is much more severe than others. Not only is it important to have a long life for the blocks, but it is necessary to have a material that will not form seeds or stones in the glass. The erosion of a typical glass tank is shown in Fig. 292 where the grooving of the blocks is evident. Recently,

good results have been obtained with blocks having a high-mullite content and low porosity. The physical characteristics of the block may perhaps be more important than the chemical composition.

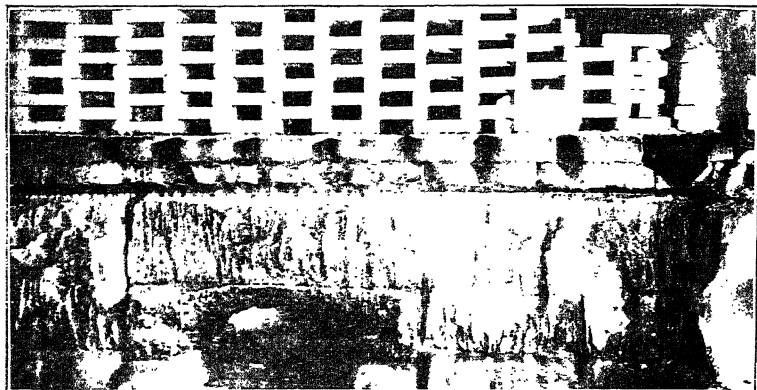


FIG. 292.—Erosion of a typical glass tank.

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CHAPTER XVI

EXPANSION AND SHRINKAGE

1. Methods of Measurement.—A number of different methods have been employed to determine the coefficient of thermal expansion of materials up to high temperatures. A few of the more satisfactory ones will be described.

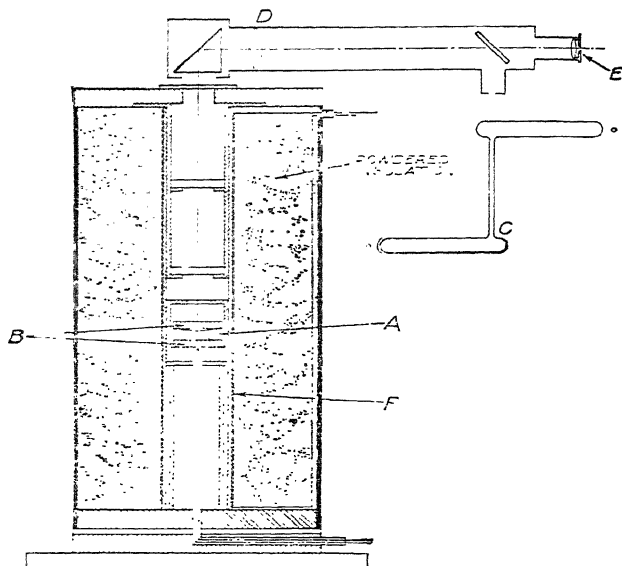


FIG. 293.—Measurement of expansion with the Fizeau interferometer.

Interferometer Method.—Where it is necessary to use a very small specimen, such as a section of glaze or enamel, the interference method, best illustrated by the Fizeau interferometer,^(8, 45, 61) is perhaps the most accurate. A cross section of this instrument is shown in Fig. 293. The specimen *A* can be in the form of a short cylinder or in three struts of equal length separating two fused quartz disks *B*, which have been polished with optically plane surfaces. Light from the vacuum tube *C* is passed through

the optical system *D* and down through the quartz-disk assembly. Light is reflected from the surfaces in contact with the specimen, and the resulting beam is passed back through the optical system to the eyepiece *E*. A series of alternating dark and light bands are produced by interference. The position of these bands is dependent upon the relative distance between the two quartz disks, and each band represents a distance of one-half wave length of the particular light used. Of course, the more nearly parallel the plates the broader will be the bands.

When a test is made, the specimen is put in place and the instrument carefully lined up until the bands appear in the field. The heater *F* is turned on, and the temperature slowly raised to any desired value while the number of bands passing a vertical cross hair in the eyepiece are counted. From the number of bands and the wave length of the light, the coefficient of thermal expansion of the specimen can be readily computed. The upper temperature is limited by this method to about 1000°C. (about 1830°F.).

Counting the passage of the bands visually is a tedious process. Also there is the danger of missing one or more bands. Recently, several devices have been used to simplify the observation. In one case, an image of the bands and crossline is thrown on a moving strip of film, giving a set of lines as shown in Fig. 294. The number of lines and fractions crossing the reference line can readily be counted. Another method consists of using several band systems from sources having different wave lengths. By an initial and final reading on three sets of bands, the expansion can be computed without a continuous count. Since considerable manipulative skill is required to obtain good results with this instrument, it is not adapted to general plant use.

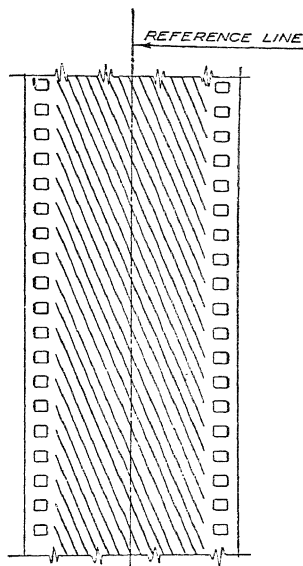


FIG. 294.—Interference bands taken on a moving-picture film.

Fused-quartz-tube Method.—Another method, which will permit tests to be made at slightly higher temperatures, consists of forming the specimen into a small cylinder and placing it in a quartz tube surrounded by a heater. The expansion of the cylinder is transferred outside the furnace by a fused quartz rod, the movement of which is measured by a micrometer telescope or dial.⁽³⁰⁾ Expansions can be measured in this way to temperatures as high as 1100°C. (about 2010°F.).⁽³¹⁾ Other experimenters have used fused-quartz distance pieces to convey the movement to a dial micrometer. Such a device was used by Geller and Heindl.⁽¹⁸⁾

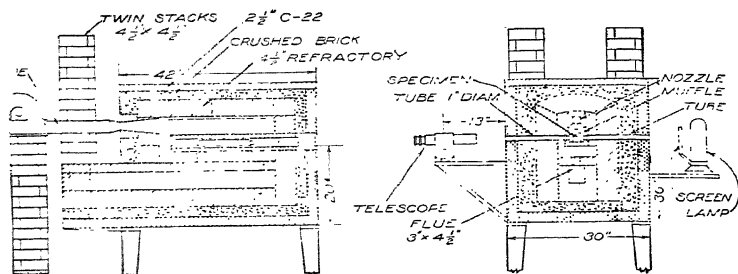


Fig. 295.—Furnace used to measure the coefficient of expansion of refractories.

A similar method is used by Heindl⁽⁴⁶⁾ in a reducing atmosphere, where graphite can replace the fused quartz and thus allow the attainment of much higher temperatures. Distance pieces of white ware body were used by Geller and Bunting.⁽⁶³⁾

High-temperature Measurements.—When it is desired to obtain the coefficient of thermal expansion of a specimen at higher temperatures, a somewhat different procedure must be followed. A method developed at the Babcock & Wilcox laboratory⁽¹¹⁾ has proved quite satisfactory up to a temperature of 1700°C. (about 3095°F.). A specimen 9 in. long and 1 in. square is evenly heated, and its length measured directly with micrometer telescopes.

A drawing of the furnace is shown in Fig. 295. The specimen is placed on a level bed of loose sand composed of some refractory material, such as fused alumina. Around the specimen is a silicon carbide muffle, which ensures an even heating of the specimen. The heat is supplied to the furnace by a gas burner, the flame passing over the muffle and down around it to the exit flue and then out through the two stacks. Sight tubes pass

through the furnace at the ends of the specimens and are cemented tightly to the walls of the muffle. The telescopes are sighted through these tubes across the ends of the specimen. Because of the excellent black-body conditions in the muffle, it would be quite impossible to distinguish the end of the specimen from the wall, so the sight tube is continued through on the other side of the furnace, and a powerful electric light with a ground-glass screen is placed at the end of the tube in order to provide a background brighter at all temperatures than the end of the specimen. The background must have an effective temperature higher than the highest reached by the specimen in order to give contrast. The light should be used for all readings, for there is an apparent shift in the image when a dark background is used.

A specimen can be cut out of a standard brick with a carborundum saw; or where a brick is not available, it can be molded and burned.

To obtain an accurate reading on the end of the specimen, it is necessary to grind and polish it accurately. The telescopes contain vertical cross hairs which can be adjusted to correspond to the image of the specimen. The temperature of the specimen for the lower range is measured with a thermocouple laid against the specimen. At high temperatures, this couple is pulled out and the temperature measured by an optical pyrometer through the sight tube. When making a test, it has been found most satisfactory to increase the temperature at a regular rate of $100^{\circ}\text{C. per hr.}$ and to make measurements of the length as often as seems desirable.

This method will give a precision of measurement within ± 0.01 per cent of the length of a specimen, and the temperature can be read to $\pm 10^{\circ}\text{C.}$ ($\pm 18^{\circ}\text{F.}$) up to the highest temperatures. The maximum temperature of this test is limited mainly by the reaction of the specimen with its support. If the expense of building a complete furnace of the test material is justified, this reaction could be prevented and temperatures as high as 1800°C. (about 3270°F.) could undoubtedly be reached.

A similar type of furnace heated by globars is more convenient to operate and control than the preceding setup but is limited in maximum temperature to about 1600°C. (about 2900°F.).

The results from expansion tests are most conveniently plotted with the temperatures as abscissas and the percentage expan-

sions as ordinates. From the slope of this curve, the coefficient of thermal expansion can be readily found at any temperature.

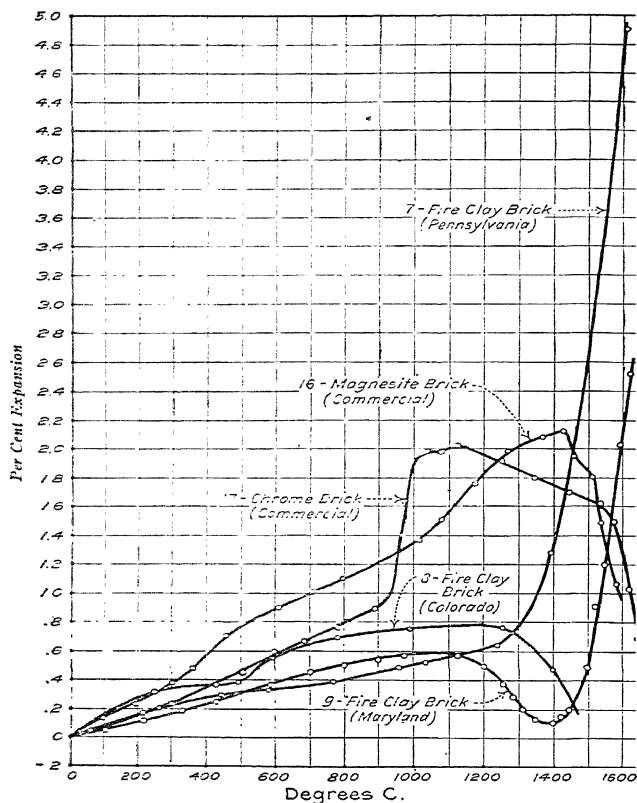


FIG. 296.—Expansion curves for a number of refractories. (J. Am. Ceram. Soc.)

2. Expansion Characteristics of a Number of Refractory Bricks.—In Figs. 296 to 300 are shown the expansion curves for a number of refractory materials. It should be kept in mind that the burning temperature markedly influences the curves, especially the temperature at which permanent shrinkage begins.

In Table 70 are summarized the main characteristics of many of these materials.

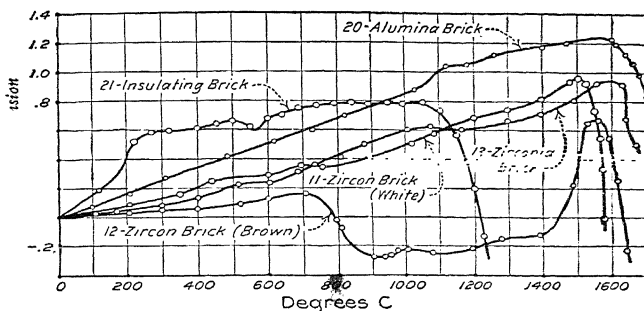


Fig. 297.—Expansion curves for a number of refractories. (J. Am. Ceram. Soc.)

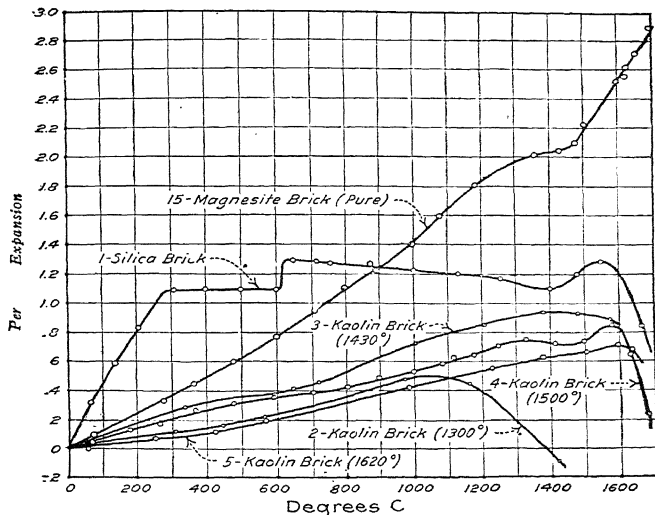


Fig. 298.—Expansion curves for a number of refractories. (J. Am. Ceram. Soc.)

The data from expansion curves are of considerable value in determining the characteristics of a brick produced from a given material. It has been shown that the tendency of a brick to

spall, other conditions being invariable, is proportional to the coefficient of thermal expansion at the temperature where spalling occurs. This temperature range lies between 300°C. (572°F.) and 700°C. (1292°F.) in most cases; hence, the maximum coefficient of expansion in this range is a direct indicator of the spall-resisting properties of the material.

The expansion curves indicate in most cases when an allotropic change takes place in the crystal structure; e.g., the curve for

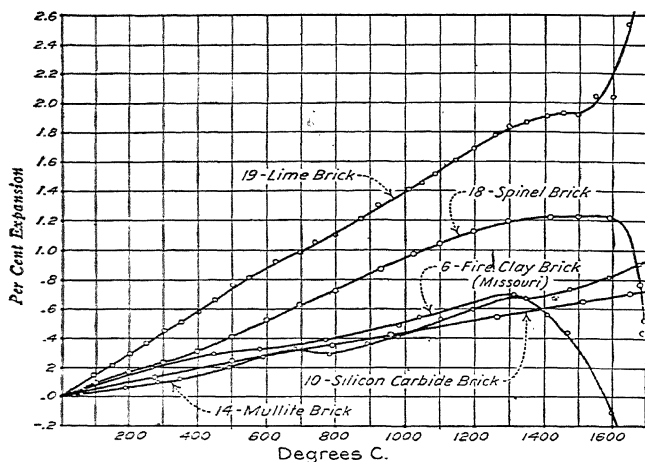


Fig. 299.—Expansion curves for a number of refractories. (J. Am. Ceram. Soc.)

the silica brick shows distinctly the inversion of low- to high-cristobalite around 260°C. (500°F.). The quartz inversion point is also sharply defined at 573°C. (1062°F.). The expansion of the specimen above 1470°C. (2678°F.) shows the gradual change of tridymite to cristobalite. The inversion point of quartz is shown to some extent in nearly all the fireclay bricks, indicating the presence of some free quartz in all these materials.

3. The temperature at which the specimen begins to shrink or expand irreversibly is of considerable importance, for it shows the approximate temperature at which the specimen is burned and also the maximum temperature at which it can be used satisfactorily in service.

The total reversible expansion of a material is of interest for the computation of the necessary expansion joints in the design of furnaces and kilns.

The effect of burning temperature on the coefficient of thermal expansion of clays is illustrated by the curves for kaolins. At the

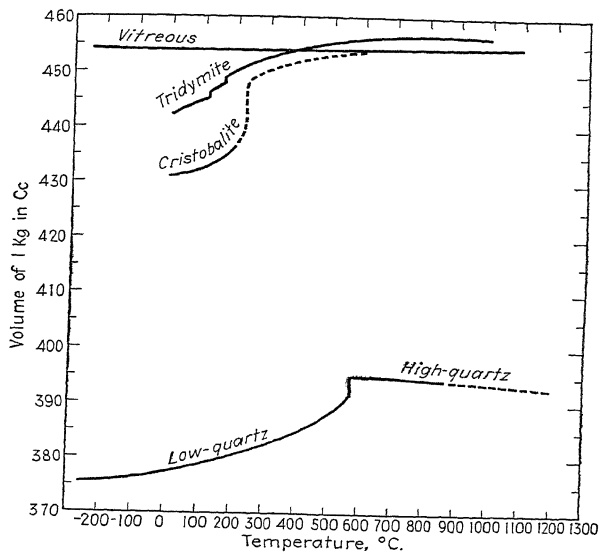


FIG. 300.—Temperature-volume curves for the principal forms of silica. (R. B. Sosman, "The Properties of Silica," Chemical Catalog Company, Inc., Reinhold Publishing Corporation, New York, 1927.)

lowest temperature, the coefficient is low owing to the small amount of mullite development and corresponding small silica formation. Only a slight trace of the silica inversion points is present. At a burning temperature of 1430°C . (2606°F .), the thermal-expansion coefficient is much higher and the inversion points are quite prominent as a result of the breaking down of the silicates to form mullite and some free silica. At 1500°C . (2732°F .), the coefficient is reduced because of the initial combination of the free silica into glass. At 1620°C . (2948°F .), the free silica has almost entirely changed to glass, giving a low coefficient.

TABLE 70.—THERMAL EXPANSION

Specimen No.	Brick type	Burning temperature		Mean coefficient of expansion between 0°F. (32°F.) and shrinkage temperature (per 1°F.)	Maximum coefficient of expansion between 300°F. (572°F.) and 700°F. (1292°F.) (per 1°F.)	Maximum irreversible contraction between 1700°F. (3092°F.) and (— is expansion)	Inversion points		Temperature at which shrinkage or expansion begins
		°C.	°F.				°C.	°F.	
1	Silica	1300	2372	0.000083	0.000100	1	240 to 610	500 to 1130	1550
2	Kaolin	1300	2372	0.000047	0.000079	1	260 to 600	500 to 1130	1050
3	Kaolin	1450	2642	0.000068	0.000087	1	260 to 600	500 to 1112	1380
4	Kaolin	1500	2732	0.000053	0.000070	1	260 to 600	500 to 1112	1380
5	Kaolin	1620	2918	0.000043	0.000067	1	—	—	1610
6	Fireclay (Missouri)	—	—	0.000051	0.000080	Large	600	1112	1300
7	Fireclay	—	—	0.000051	0.000061	—5	600	1112	1250
8	Fireclay (Colorado)	—	—	0.000051	0.000074	Large	260 to 600	500 to 1112	1250
9	Fireclay (Maryland)	—	—	0.000015	0.000080	—3	—	—	1100
10	Silicon carbide	—	—	0.000013	0.000018	—	800	1472	1700+
11	Zircon (white)	1650	3002	0.000041	0.000062	Large	600 to 1400	1112 to 2552	1510
12	Zircon (brown)	1500	2804	0.000042	0.000048	2	800 to 1150	1472 to 2162	1540
13	Zirconia	1675	3047	0.000053	0.000087	1	780 to 1350	1436 to 2462	1600
14	Mullite	1785	3245	0.000053	0.000082	0	1430	2606	1700+
15	Magnesite (pure)	1680	3056	0.000142	0.000151	0	—	—	3092+
16	Magnesite (Com'l)	—	—	0.000147	0.000210	2	1000	1832	3092+
17	Chrome (Com'l)	—	—	0.000164	0.000121	2	—	—	1440
18	Spinel	1690	3074	0.000076	0.000110	1	1500	2732	1600
19	Lime	1740	3164	0.000138	0.000115	0	200 to 570	500 to 1050	1512
20	Alumina	1650	3002	0.000077	0.000082	0	—	—	1700+
21	Insulating	—	—	0.000074	0.000180	1	1180	2156	1380
22	Zircon (electrically fused)	—	—	0.000042	0.000140	Large	—	—	2876
23	Magnesite (electrically fused)	—	—	0.000102	0.000120	—	—	—	3092+
24	Topaz	1675	3047	0.000043	0.000151	—	—	—	1580
25	Zircon (purified)	—	—	0.000038	0.000151	—	—	—	1922

It may be concluded that magnesite, chrome, and lime have high mean coefficients of thermal expansion. Silica, alumina, and spinel have intermediate values, whereas clays, zirconia minerals, mullite, and silicon carbide generally have low values. In regard to the coefficient of expansion in the spalling range, silica shows much the highest value. Magnesite, chrome, lime, and spinel also have high values, as their sensitiveness to spalling would lead us to believe. Clays, alumina, mullite, zirconia minerals, and silicon carbide have lower values.

The more recent results of Heindl⁽⁴⁶⁾ made in a reducing atmosphere are substantially the same as those given above, except in the case of chromite where a difference was noted.

3. Expansion of Silica Minerals.—The thermal-expansion characteristics of the various forms of silica are of interest, because the inversion points are clearly shown. An expansion curve of a silica refractory will indicate roughly the constituents present. In Fig. 300 are shown expansion curves of the four forms of silica. The low expansion of the quartz glass and the sudden changes at the inversion points are noteworthy. As discussed in Chap. IV all of the high temperature forms of silica have a low coefficient of expansion.

The volume of all forms of silica is comparatively constant above 600°C. (1112°F.); therefore no spalling troubles will be encountered if the furnace is never allowed to fall below this temperature. Open-hearth steel furnaces, for example, which are constructed to a considerable extent of silica brick, experience large and sudden temperature changes. The temperature, however, is never allowed to fall below 600°C. (about 1110°F.) or 800°C., (about 1470°F.) even for repairs.

Unfortunately, quartz glass is not stable above about 1200°C. (about 2190°F.). If it were, a refractory extremely resistant to temperature changes could be made of it.

4. Coefficient of Thermal Expansion of Other Refractory Materials.—In Table 71 are given the coefficients of thermal expansion of a number of other refractory materials. A discussion of the connection between coefficient of thermal expansion and atomic structure is given in Chap. IV.

5. Reheat Shrinkage of Refractories.—To determine the fitness of a particular brick for service, it is often tested for shrinkage under temperature conditions equivalent to those which it would

TABLE 71.—COEFFICIENT OF THERMAL EXPANSION OF HIGH-FUSING CRYSTALS

Material	Temperature range		Coefficient of thermal expansion per °C	Authority
	°C.			
Alumina, fused, recrystallized	25-800	77-1472	7.9×10^{-6}	Merritt ⁽⁸⁾
Sapphire, principal axis	20-1000	68-1832	9.0	Austin ⁽⁵⁹⁾
Sapphire, \perp principal axis	20-1000	68-1832	8.3	Austin ⁽⁵⁹⁾
Magnesium oxide, fused	25-800	77-1472	13.4	Merritt ⁽⁸⁾
Magnesium oxide, single crystal	25-1000	77-1832	13.8	Austin ⁽⁵⁹⁾
Mullite, aggregate	20-1430	68-2552	5.3	Heindl ⁽⁴⁶⁾
Mullite, principal axis	20-1000	68-1832	5.7	Austin ⁽⁵⁹⁾
Mullite, \perp principal axis	20-1000	68-1832	4.5	Austin ⁽⁵⁹⁾
Zircon, principal axis	20-800	68-1472	6.2	Austin ⁽⁵⁹⁾
Zircon, \perp principal axis	20-800	68-1472	3.7	Austin ⁽⁵⁹⁾
Zirconia, principal axis	25-800	7-1472	8.1	Merritt ⁽⁸⁾
Zirconia, \perp principal axis	25-800	7-1472	7.3	Merritt ⁽⁸⁾
Zirconia, aggregate	25-800	7-1472	6.2	Merritt ⁽⁸⁾
Zirconia, principal axis	20-900	68-1652	5.7	Austin ⁽⁵⁹⁾
Zirconia, \perp principal axis	20-900	68-1652	8.9	Austin ⁽⁵⁹⁾
Chromite, single crystal	20-1000	68-1832	8.1	Austin ⁽⁵⁹⁾
Thoria, aggregate	25-800	77-1472	9.3	Merritt ⁽⁸⁾
MgO-Al ₂ O ₃ aggregate	25-800	77-1472	8.9	Chesters and Parmelee ⁽⁴⁹⁾
MgO-Al ₂ O ₃ aggregate	25-800	77-1472	8.0	Chesters and Parmelee ⁽⁴⁹⁾
FeO-Al ₂ O ₃ aggregate	25-800	77-1472	8.6	Chesters and Parmelee ⁽⁴⁹⁾
MnO-Al ₂ O ₃ aggregate	25-800	77-1472	7.1	Chesters and Parmelee ⁽⁴⁹⁾
ZnO-Cr ₂ O ₃ aggregate	25-800	77-1472	10.1	Chesters and Parmelee ⁽⁴⁹⁾
MgO-Cr ₂ O ₃ aggregate	25-800	77-1472	9.3	Chesters and Parmelee ⁽⁴⁹⁾
FeO-Cr ₂ O ₃ aggregate	25-800	77-1472	8.5	Chesters and Parmelee ⁽⁴⁹⁾
MnO-Cr ₂ O ₃ aggregate	25-800	77-1472	9.2	Chesters and Parmelee ⁽⁴⁹⁾
ZnO-Fe ₂ O ₃ aggregate	25-800	77-1472	9.7	Chesters and Parmelee ⁽⁴⁹⁾
MgO-Fe ₂ O ₃ aggregate	25-800	77-1472	12.7	Chesters and Parmelee ⁽⁴⁹⁾
FeO-Fe ₂ O ₃ aggregate	25-800	77-1472	15.5	Chesters and Parmelee ⁽⁴⁹⁾
MnO-Fe ₂ O ₃ aggregate	25-800	77-1472	11.0	Chesters and Parmelee ⁽⁴⁹⁾
90 per cent cordierite, aggregate	20-308	68-586	1.0	Geller and Insley ⁽⁴³⁾
80 per cent forsterite, aggregate	20-304	68-579	8.3	Geller and Insley ⁽⁴³⁾
Beryl, principal axis	20-300	68-572	2.2	Geller and Insley ⁽⁴³⁾
Beryl, principal axis	20-265	68-509	1.0	Geller and Insley ⁽⁴³⁾
95 per cent zinc orthosilicate	20-350	68-662	1.6	Geller and Insley ⁽⁴³⁾
Zinc aluminate	20-525	68-977	7.7	Geller and Insley ⁽⁴³⁾
Celsian, 90 per cent	20-400	68-752	3.4	Geller and Insley ⁽⁴³⁾
Anorthite, 95 per cent	20-300	68-572	4.3	Geller and Insley ⁽⁴³⁾

receive in use. This aftershrinkage may be determined by the bar method, as described earlier in this chapter, which has the advantage of giving a continuous record of the shrinkage throughout the range of temperatures, but often it is desirable to make a test on a whole brick.

This is done by first determining the length or volume of the brick by measurement and then subjecting it to a prolonged

TABLE 72.—CHANGE IN LINEAR DIMENSIONS ON REHEATING*

Brick	Per cent of change after heating	
	5 hr. at 1400°C. (2557°F.)†	5 hr. at 1500°C. (2732°F.)
Pennsylvania.....	0.7	2.1
	-0.6	
	0.1	
	0.3	
	1.3	
	0.1	
	-1.6	
	0.8	
	0.3	
	0.2	
	0.1	
	-1.8	
	-0.2	
	1.1	
	1.4	
Missouri.....	-0.3	-0.4
	-0.8	-0.7
	0.3	
	0.8	
	-0.2	
	0.1	
	-0.1	
	-0.2	
	-0.2	
	-0.1	
	-0.4	
Kentucky.....	1.7	4.5
California.....	0.0	
	-0.2	
	0.0	
Maryland.....	0.2	
	0.3	
	0.3	
	0.0	
	0.3	
Colorado.....	-0.7	-1.2
New Jersey.....	0.1	-0.8
New Jersey.....	0.2	-1.7

* Heat Measurements Laboratory, Massachusetts Institute of Technology.

† Negative sign indicates shrinkage.

heating at the desired temperature. After the brick is cooled, it is again measured and the length, volume, and shrinkage determined.

The standard A.S.T.M. test for reheat shrinkage is as follows:

STANDARD METHOD OF TEST FOR PERMANENT LINEAR
CHANGE AFTER REHEATING OF REFRACTORY BRICK

A.S.T.M. Designation: C 113-36¹

ADOPTED, 1936

This Standard of the American Society for Testing Materials is issued under the fixed designation C 113; the final number indicates the year of original adoption or, in the case of revision, the year of last revision.

1. **Scope.**—This method of test covers a procedure for determining the permanent linear change of certain types of refractory materials when heated under prescribed conditions.

2. **Apparatus.**—The apparatus shall consist of a kiln of the down-draft type and of such design as not to permit the flame to impinge directly from the burner upon the test specimens. The kiln atmosphere during the test shall be kept as oxidizing as is practicable.

3. **Test Specimens.**—*a.* The test specimens shall consist of three standard 9-in. brick ($9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ in.) or three pieces of these dimensions cut out of larger shapes.

b. Each test specimen shall be labeled with ceramic paint and carefully measured for length before and after reheating. The measurements shall be made by the use of a firm joint caliper and a steel rule. The calipering shall be done at the center of each end, and the dimension shall be measured to the nearest 0.02 in., or 0.5 mm.

4. **Location of Test Specimens in Kiln.**—The test specimen shall be placed in the kiln so that each will rest on a 9 by $2\frac{1}{2}$ -in. face and only one course high. Each specimen shall be placed upon the 9 by $2\frac{1}{2}$ -in. face of a supporting brick which shall be from the same lot as the test specimen or at least of equal refractoriness. There shall be placed between the test specimen and the supporting brick a layer of calcined diaspore, kyanite, or fused alumina ground to pass a No. 20 (840 μ) A.S.T.M. sieve (equivalent to mesh No. 20 of the Tyler standard series). Each specimen shall be placed so as to be not closer than $1\frac{1}{2}$ in. from other test specimens or the furnace wall.

5. **Temperature Measurement.**—*a.* The temperature within the kiln shall be measured by means of a platinum-platinum-rhodium thermocouple and a pyrometer, preferably a recording pyrometer. The hot junction of the couple shall be placed so as to register the temperature

¹ A.S.T.M. Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

of the test specimens. The kiln shall be of uniform temperature over the hearth and shall be checked from time to time by means of cones, and they shall not show a difference of more than one cone. Above 1450°C., the thermocouple should be withdrawn and an optical pyrometer shall be used. The sighting shall be directed upon one of the test specimens.

b. During the constant temperature period of the test, the temperature as measured by the thermocouple shall not be allowed to vary by more than $\pm 10^{\circ}\text{C.}$ and, in the case of the optical pyrometer, $\pm 15^{\circ}\text{C.}$ Temperature readings shall be made at intervals not greater than 15 min.

6. **Test Temperature Schedules.**—The kiln shall be operated so as to conform to the temperature schedule specified for the particular test to be conducted. Heating schedules for various classes of refractories are shown in the following table:

HEATING SCHEDULE FOR REHEAT TEST OF VARIOUS TYPES OF REFRACTORIES

Elapsed time from start of heating, hr.	Temperature of test specimen, °C.			
	Schedule A	Schedule B	Schedule C	Schedule D
1	Between 700–800	Between 900–1000	Between 900–1000	Between 825 and 925
2	Between 1075–1125	Between 1275–1325	Between 1275–1325	Between 1225 and 1275
3	1200 \pm 10 maintained for 5 hr.	1400 \pm 10 maintained for 5 hr.	Between 1450–1500	1350 \pm 10 maintained for 5 hr.
4			Between 1550–1575	
5			1600 \pm 15 maintained for 5 hr.	

7. **Cooling.**—After completion of the heating period the test specimens shall be allowed to cool in the closed kiln for a period of at least 10 hr.

8. **Calculation.**—The test specimens shall be remeasured after rubbing the ends with an abrasive block to remove small blisters. The percentage linear change based upon the original length shall be calculated and reported as the average value of the three test specimens.

In Table 72 are given some values for typical fireclay bricks under the standard test conditions. A few values are also given at 1500°C. (2732°F.). It is interesting to notice that this test indicates an expansion as often as a shrinkage. This reheat volume increase is known both as “secondary expansion” and “afterexpansion.” At the higher temperature, the shrinkage or expansion is usually increased; but in some cases, there is little change; and in others, an actual reversal in sign occurs.

Another test that determines the aftershrinkage of a brick is the simulative service test used by the U.S. Navy. According to the description by Rogers,⁽²⁸⁾ it consists in building up two

walls of a furnace, one of the brick to be tested and the other of a standard brick. The furnace is then run for 24 hr. at a temperature of 1590°C. (2900°F.) and again at 1650°C. (3000°F.), with an examination of the walls between the tests. An examination of the wall after it is cooled will indicate by the width of the open joints the approximate shrinkage of the bricks. The photographs in Figs. 301 and 302 show typical walls. This test is, of course, not quantitative, but it does more or less correspond to actual service conditions. It is believed that a wall that shrinks a small amount at each joint is better than a wall that concentrates its shrinkage into a few large cracks. It should also be realized that a wall may have a considerable amount of open joints when cool and yet be substantially tight when at a high temperature.

As previously mentioned, bricks may show either an expansion or a shrinkage when heated to the temperatures of service. In general, bricks are not burned so high in the process of manufacture as the temperature of service; consequently, with the usual type of clay, the brick will decrease in volume at service temperatures. This is undesirable, especially in crowns and arches, because the open joints resulting give corners for spalling and slag erosion to start. The open cracks also concentrate the load in the arch on a relatively small area of the block, which greatly decreases the stability of the structure. A slight expansion is not particularly harmful if the wall or arch is properly designed.

Theory of Secondary Expansion.—There are three phenomena that may produce an increase in volume of ware subjected to the reheat test. They are

1. Overfiring, *i.e.*, development of a vesicular structure, or bloating.
2. Opening of the laminations of the clay.
3. Transformations or reactions in the crystalline phases during the firing, yielding products of lower true density than the reactants.

In general, these phenomena take place in certain definite temperature ranges. When the temperature at which a brick is first fired is below this range, the brick may expand if subjected to a reheat temperature in the expansion range. When the temperature of the initial firing is in the expansion range, the ware may shrink, expand, or stay constant in volume in the reheat test, depending upon the time and the atmosphere of firing.

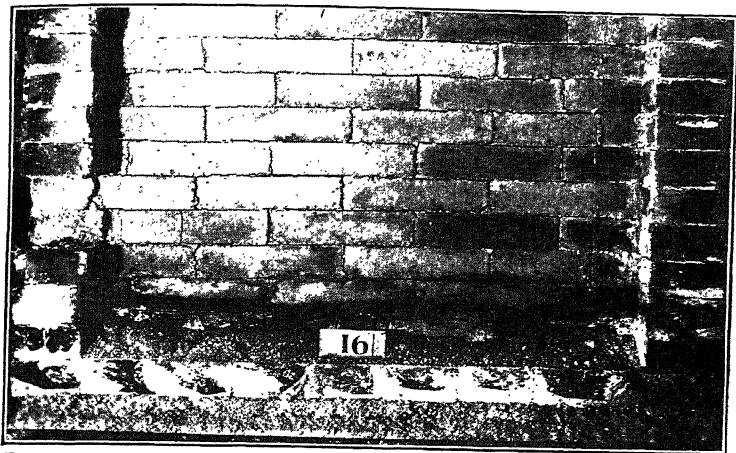


FIG. 301.—Simulative service test, after a 1650°C. (3000°F.) heat. Bricks in fair condition.

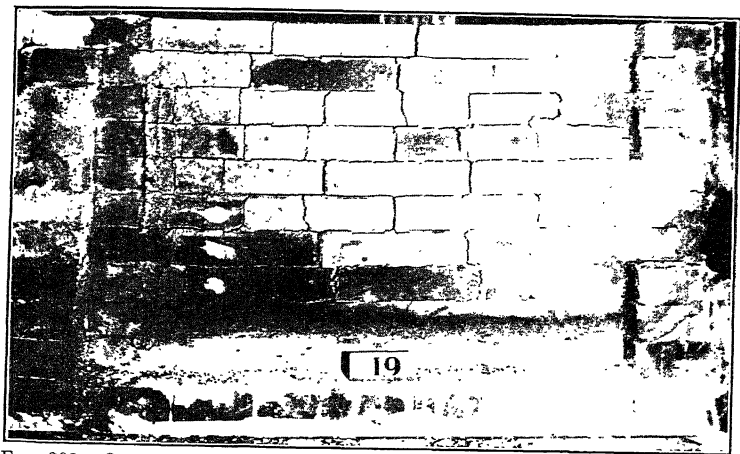


FIG. 302.—Simulative service test, after 1650°C. (3000°F.) heat. Bricks in poor condition.

The reactions that take place to cause overfiring have been discussed in Chap. IX. Overfiring occurs in certain clays, especially plastic clays, and it is probable that the decomposition of some materials, perhaps sulfides and sulfates, is inhibited so gases are not given off until a temperature near the fusion point is reached. These gases form bubbles in the glassy portion of the clay, and an expansion may result.

True secondary expansion may be caused by either 2 or 3 above. The former was investigated by Everhart,⁽⁵⁹⁾ who concluded that the increase in bulk volume was due to the opening of natural laminations or bedding planes in the clay grains. Fine grinding, blending of expanding and shrinking clays, slow firing, oxidizing atmosphere, and high forming pressure are suggested as means to decrease or eliminate the tendency to expand. This secondary expansion is characteristic of many clay deposits. The secondary expansion of the fireclay bricks given in Table 72 is undoubtedly due to the opening of the laminations in the clay grains. Reference should also be made to the paper on this subject by Heindl and Mong.⁽⁶²⁾

The discussion of the changes in kyanite during heating and the firing properties of clay-kyanite bodies in Chap. IX is an excellent example of secondary expansion due to 3 above. Referring to curve *D* in Fig. 146 of Chap. IX, it is clear that a brick of that composition fired first at about 2400°F. would show considerable expansion if reheated at 2700°F. However, if the reheat temperature were above 2950°F., shrinkage would result.

The expansion of refractories having high-alumina grog (corundum and mullite) bonded with fireclay or kaolin is due to transfer of silica into the grog grains by diffusion, which converts some of the corundum to the more bulky mullite, as clearly shown by Hall.⁶⁵

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CHAPTER XVII

HEAT TRANSMISSION BY REFRACTORIES

In certain parts of a furnace, such as the walls or roof, a minimum transmission of heat to the outside is desired; hence, a refractory with a low thermal conductivity would be necessary for these conditions. On the other hand, such parts as muffles or underfired hearths require a refractory with a high conductivity value. It will therefore be seen that the furnace designer must have accurate data on the thermal conductivity of his refractories before he can intelligently select his materials or predict the performance of his furnace.

1. Laws of Heat Conduction. *Definitions and Units.*—The following symbols have been generally adopted in reference to heat flow:

q = the quantity of heat conducted, B.t.u. per hr.

t_0 = the initial temperature in variable flow

t_1 = the temperature of the hotter surface, deg. F.

t_n = the temperature of the cooler surface, deg. F.

L = the thickness of the wall, in.

k = the conductivity of the material, B.t.u. · hr.⁻¹ · ft.⁻² · in. deg. F.⁻¹

A = the area of the section normal to the flow, sq. ft.

x = the distance from the hotter surface, in.

h^2 = the diffusivity = $\frac{k}{\rho c}$

ρ = bulk density, lb. per cu. ft.

c = the specific heat

τ = time, hr.

Table 73⁽⁶³⁾ gives factors to convert the common units of heat flow into others. Throughout this chapter, engineering units will be used.

Steady Flow.—For conditions of steady flow, the amount of heat passing through a wall is expressed by

$$q = \frac{kA(t_1 - t_n)}{L}$$

*Based on International Critical Tables; mean values used for lg.-val. and B.C.U.; from White, American Ceramic Society. (63)

or if we consider a unit area of 1 sq. ft., then

$$q = \frac{t_1 - t_n}{\frac{L}{k}} \quad (1)$$

for a simple wall.

In a composite wall made up of several layers, the value of q is obviously the same for each layer under steady conditions; therefore

$$q = \frac{t_1 - t_n}{(L_1/k_1) + (L_2/k_2) + \dots (L_n/k_n)} \quad (2)$$

where $L_1, L_2, \dots L_n$ and $k_1, k_2, \dots k_n$ refer to the properties of each layer, respectively.

Since the temperature drop across each layer is equal to the heat flow times the actual resistance of the respective layers, we may say

$$t_1 - t_2 = q \frac{L_1}{k_1} \quad (3)$$

$$t_2 - t_3 = q \frac{L_2}{k_2} \dots \quad (4)$$

From these temperature drops, the interface temperatures can be computed. It should also be remembered that the value of q entering the hot face and leaving the cool face is equal to the q of each layer.

Variable Flow.—In practice, many cases of unsteady heat flow occur, as in batch-type furnaces. In a simple case, suppose that a wall is suddenly heated from t_0 to t_1 on one face. The temperature at a point x distant from the face is given by Fourier's equation.

$$t = \frac{2t_0}{\sqrt{\pi}} \int_0^\infty \frac{x}{2h\sqrt{\tau}} e^{-\beta^2} d\beta \quad (5)$$

where β = a variable of integration

It will be seen that the penetration of heat will depend on time and the value of diffusivity. An infinite time is required theoretically to reach equilibrium, and practical equilibrium requires many hours in thick walls. In Fig. 303 are shown curves of temperature rise of the cool face in refractory walls of various thicknesses that have suddenly been heated on one face.

When the hot face is not brought up suddenly but at a definite schedule, the calculations are difficult. They may be approximated, however, by adding an imaginary layer to the hot face of the wall, as suggested by Ingersoll and Zobel,⁽¹⁾ or the Schmidt method may be used as illustrated by Trink.⁽⁵⁰⁾

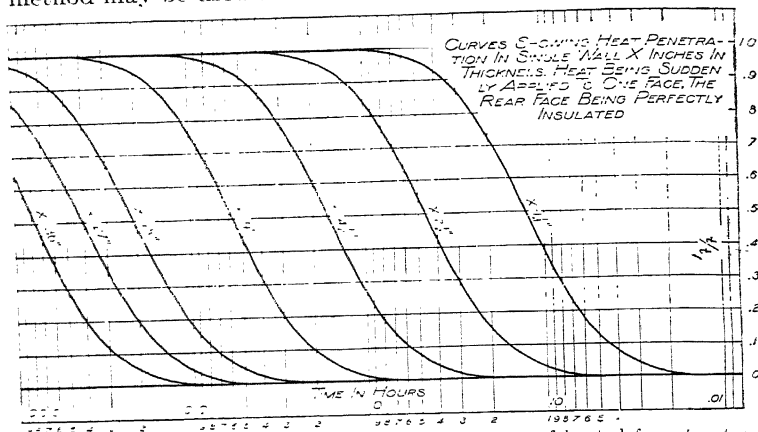


FIG. 303.—Heat-penetration curves; t_1 = temperature of heated face, t = temperature of rear face, x = wall thickness.

2. Theory of Heat Transfer through a Porous Body.—Since most refractories are more or less porous, it is of interest to see how this porosity influences the transfer rate.

Conduction.—Some of the heat is conducted through the body by virtue of the close contact of the particles making up the structure. This conduction will be decreased as the porosity increases.

Convection.—If the pores are filled with air or combustion gases, as would usually be the case, some heat is transferred by convection currents in the pore itself. This transfer is so small as to be negligible for the usual size of pores.

Radiation.—A considerable portion of the heat flow at high temperatures may be due to direct radiation across the pores. For a given amount of porosity, the large pores will transfer more heat by radiation.

The radiant heat transferred is also proportional to the emissivity of the refractory surface. These total emission coefficients

are not accurately known at high temperatures, but some figures by Heilman^(16a) indicate that a black brick such as chrome has a value of 0.97 whereas a white refractory like a kaolin brick has a value as low as 0.3.

There is an excellent opportunity for anyone interested in the field of high-temperature insulators to do some valuable work by correlating the theoretical and measured values of k for materials with various types of porosity and emissivity.

3. Measurement of Thermal Conductivity. *The High-temperature Calorimeter Method.*—Most of the high-temperature tests on refractories for thermal conductivity have been made by setting up a uniform parallel flow of heat normal to the faces of a slab. The quantity of heat flowing is measured by a water calorimeter on the cold face of the specimen, and the temperature gradient by the thickness and hot- and cold-face temperatures.

The establishment of a uniform flow is by no means easy, and only by careful guarding can this be accomplished. Also the temperatures on the isothermal planes must be read with great care. At the same time, an equilibrium flow must be established by a constant hot-face temperature for a long time interval. Perhaps no other physical measurement is beset with so many pitfalls.

This method can best be explained by an example of a high-temperature plate tester originally suggested by Professor Wilkes but later constructed in many laboratories with minor changes. The following description applies to an apparatus recently constructed in the refractories laboratory of the Babcock and Wilcox Company.

A drawing of this apparatus is shown in Fig. 304. The specimen a rests on the calorimeter b and guard ring c . The last-mentioned is surrounded by a cooling coil d to prevent heat from passing to the underside of the calorimeter. The heat is supplied by a grid of globar heaters e in the upper chamber f lined with insulating firebrick. A silicon carbide slab r distributes the heat evenly. The hot- and cool-face temperatures are measured by the thermocouples g and h , and an intermediate temperature by couple i . The temperature rise in the calorimeter is measured by multiple differential couples j in the inlet and outlets. The differences in temperature between the guard ring and calorimeter are also measured by multiple differential

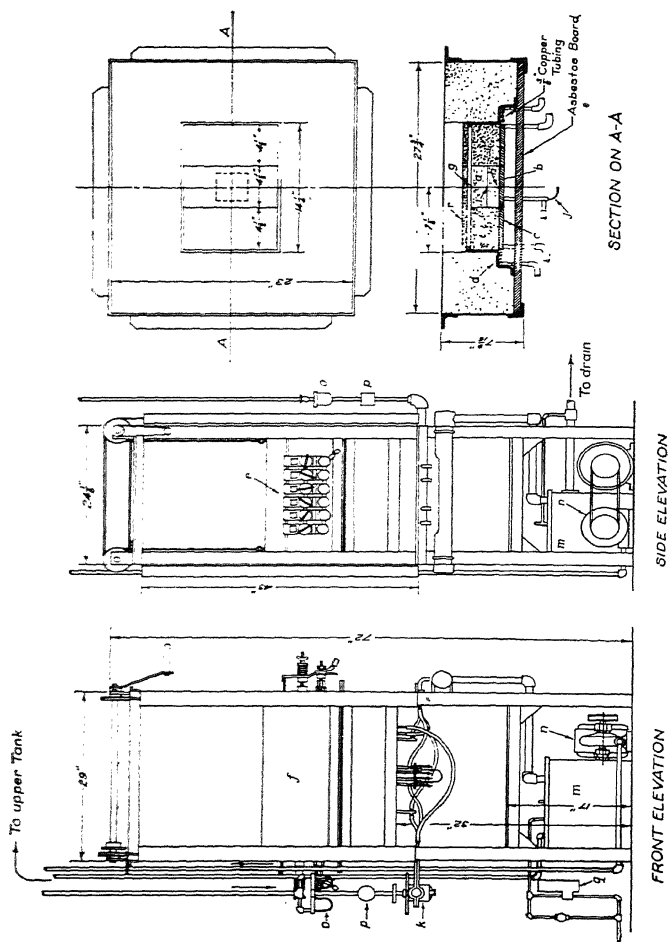


FIG. 304.—High-temperature thermal-conductivity apparatus. This apparatus, with minor changes, has been adopted as a tentative standard by the American Society for Testing Materials.

couples imbedded in the metal. The water flow is controlled by special regulating valves *k*. The water for the calorimeter and guard is circulated by the pump *n* between the upper tank *l* and the lower tank *m*. This keeps it free from air, and the filter *o* removes any sediment. The water in the lower tank is cooled by a copper coil through which tap water flows. The temperature of the water entering the calorimeter is held constant by

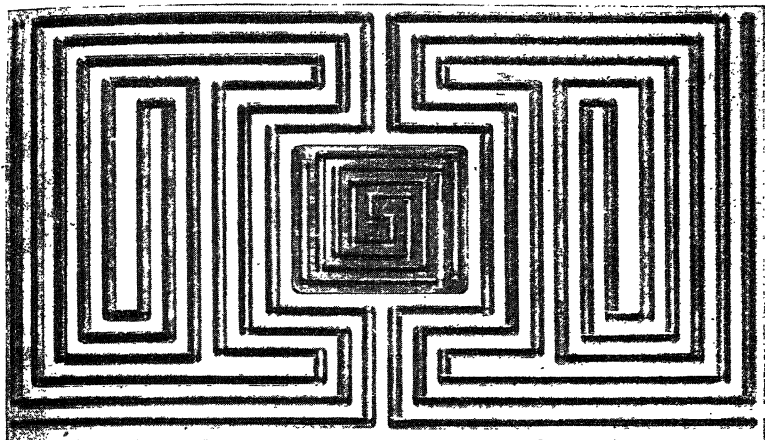


FIG. 305.—Water passages in the calorimeter and guard ring.

the thermostat *p* and the control valve *q*. In Fig. 305 is shown the arrangement of water passages in the calorimeter and guard ring.

Special features are the constant-temperature water source, the temperature control of the furnace to maintain the temperature for the 24-hr. run within $\pm 2^{\circ}\text{F.}$ and the flow passages in the calorimeter. The method of making a test will be made clear by the following example of a run made on an insulating firebrick in Table 74.

Thermal conductivity is measured in other ways; *e.g.*, a cylindrical specimen is sometimes convenient as shown in Fig. 306 which represents a pipe cover tester. In this way, edge losses are minimized, because the area of the ends is small compared with the outside area; but it is often difficult to obtain standard

TABLE 74.—TYPICAL THERMAL-CONDUCTIVITY RUN

Time	Difference between guard and calorimeter, M.V.	Difference between inlet and outlet of calorimeter, M.V.	Hot face, M.V.	Center, M.V.	Cold face, M.V.	Water flow, per cc. min.
9:00	0.002	0.030	4.62	13.73	1.70	
10:00	0.000	0.028	4.83	13.93	1.79	360
10:40	0.000	0.030	4.72	13.77	1.70	358
11:00	0.000	0.029	4.76	13.79	1.72	361
11:30	0.000	0.029	4.65	13.76	1.68	370
12:34	0.000	0.029	4.62	13.67	1.68	367
1:45	0.000	0.027	4.63	13.64	1.67	360
2:15	0.000	0.028	4.63	13.65	1.68	
3:15	0.000	0.027	4.63	13.66	1.67	360
	= 0°F.	= 0.24°C.	= 995°F.	= 630°F.	= 105°F.	

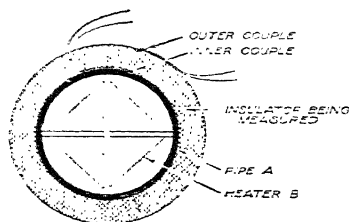
$$q = 0.24 \times 3.83 \times 360 = 332 \text{ B.t.u. per hr.}$$

$$\frac{332 \times 1.25}{630 - 105} = \frac{414}{525} = 0.79 = k \text{ at } 368^\circ\text{F.}$$

$$\frac{332 \times 2.5}{995 - 105} = \frac{830}{890} = 0.93 = k \text{ at } 550^\circ\text{F.}$$

$$\frac{332 \times 1.25}{995 - 630} = \frac{414}{365} = 1.13 = k \text{ at } 812^\circ\text{F.}$$

refractories of the proper shape. The cylindrical method, however, has been used by Holler³³⁰ and others for high-temperature tests.



306.—Pipe tester for measuring thermal conductivity.

The Northrup method consists in passing a uniform, linear flow of heat through two layers of refractory in contact. If the temperature drop is known through each layer and the value of k known for one material, the conductivity of the other layer can be readily determined, as the value of q

must be the same for both. The following relation holds:

$$\frac{\text{Temperature drop in specimen } A}{\text{Temperature drop in specimen } B} = \frac{k_B}{k_A}$$

Harmonic-flow Method.—A somewhat different method has been used to determine the thermal conductivity by making use of Fourier's equation for nonuniform heat flow. If we consider Eq. (5) in this chapter, it will be noticed that the value of h^2 , the diffusivity, can be determined by studying the temperature changes in a given material. From the value of h , the thermal conductivity can be computed if the density and specific heat are known, properties that are not difficult to measure. This method has been carried out practically by applying to one surface of the test material a temperature varying harmonically. The temperature is then recorded inside the solid at several distances from the surface; and from these values, h can be computed. It will be noticed that this method does not necessitate a measurement of the quantity of heat flowing. On the other hand, the same difficulties are encountered in ensuring a linear flow of heat as in the other methods, and the problem of providing a sinusoidal heat supply at high temperatures is a serious one.

4. Thermal-conductivity Values for Refractories and Insulators. *Crystals and Glasses.*—The available data for crystals and glasses are very meager at low temperature and nonexistent at high temperatures. A few values are shown in Table 75 to bring out three important facts: (1) The thermal conductivity for some crystals decreases with increasing temperature, probably reaching a minimum and then increasing again, whereas for glasses it always increases. (2) The k value for a crystal with an orderly arrangement of atoms is greater than that for a corresponding glass as shown for the case of silica. (3) The conductivity of nonisotropic crystals varies with the direction of heat flow, being a maximum along one principal axis and a minimum along another. The ratio of the maximum and minimum k for a number of crystals is shown in the last column of Table 75.

At present, there are insufficient data to formulate a relation between atomic structure and thermal conductivity with any certainty. However, the following equation proposed by Comp-ton⁽⁶⁵⁾ seems best to fit the experimental results.

$$k = bn^2dRv \cdot \frac{2 - cT^{1/2} \cdot e^{-Bv/2T}}{c^2T}$$

where $b = 1$

n^2 = number of atoms per unit area of the plane normal to the heat flow

d = distance between neighboring atoms

v = the natural frequency of the atoms

c = determined by the conductivity at a given temperature

B = universal constant

There are a number of other references on computation of thermal conductivity some of which have been referred to on page 80.

TABLE 75.—THERMAL CONDUCTIVITY OF CRYSTALS AND GLASS

Material	Mean thermal conductivity at a mean temperature of			Ratio of minimum k to maximum k
	0°C.	100°C.	200°C.	
Quartz parallel to axis.....	102.0	73.0	61.0	0.57
Quartz perpendicular to axis.....	52.0	41.0	38.0	
Vitreous silica.....	9.3	11.0	12.5	
Soda-lime glass.....	7.9			1.00
Pyrex glass.....	7.0		8.2	1.00
Zircon.....				0.81
Topaz.....				0.94
Beryl.....				0.81
Rutile.....				0.62
Corundum.....				0.85

The field of research connecting thermal conductivity with atomic structure is almost virgin territory and offers excellent opportunity for further work, especially in developing a precise method of measuring k up to high temperatures on very small specimens.

Heavy Refractories.—The commercial refractory consists of crystalline material alone or with a glass bond. Usually the crystals are small and randomly oriented. We would expect, from the preceding data, that the value of k would be higher for those refractories consisting of well-bonded crystals with the glass phase eliminated. For example, the recrystallized silicon carbide contains very little glass and has a high conductivity value. A great deal more research is needed on the

conductivity of refractories made of crystals, glass, and air in varying proportions. Some values of thermal conductivity of heavy refractories are shown in Table 76. Owing to experimental

TABLE 76.—HEAVY REFRACTORIES
Mean Thermal Conductivity* at a Mean Temperature, Deg. F.

Type of brick	Porosity, per cent	400	800	1200	1600	2000	2400	Authority
Alumina, fused.....	21.3	18.5	21.7	24.2	26.7	28.4	30.0	Norton ⁽²⁶⁾
Carbon.....					18.5	22.0		Powell and Schofield ⁽⁶⁴⁾
Chrome.....	30.5	10.0	10.8	11.3	11.6	11.8	12.0	Norton ⁽²⁶⁾
Fireclay.....	{ 15.2	8.1	8.4	10.1	10.8	11.4	12.0	Wilkes ⁽⁴⁴⁾
	{ 18.4	7.3	8.7	9.8	10.6	11.6	11.8	Norton ⁽²⁶⁾
	{ 26.7	7.0	7.8	8.7	9.3	10.2	10.5	Norton ⁽²⁶⁾
Graphite.....		730	500	400	310	220		Powell and Schofield ⁽⁶⁴⁾
Kaolin.....	{ 10.8	13.5	15.0	16.3	18.0	18.8	19.7	Norton ⁽²⁶⁾
	{ 23.2	10.0	10.9	11.9	12.8	13.4	13.8	Norton ⁽²⁶⁾
	{ 49.1	3.0	4.4	5.2	6.1	6.7	7.1	Norton ⁽²⁶⁾
Magnesite.....	{ 29	25.8	22.0	18.2	15.7	13.7	12.6	Wilkes ⁽⁴¹⁾
	{ 31.6	39.2	35.2	29.0	26.7	25.6	25.0	Norton ⁽²⁶⁾
Silicon carbide clay <i>b</i>	28.3	26	26	29	34	38	50	Wilkes ⁽⁴⁴⁾
Silicon carbide clay 5 per cent.....	16.2		175	155	135	118		Holler ⁽⁵⁵⁾
Silicon carbide clay 20 per cent.....	21.0		70	61	58	57		Holler ⁽⁵⁵⁾
Silicon carbide, re- crystallized	{ 34.4	210	175	150	115	95	81	Wilkes ⁽⁴⁴⁾
	{ 35.3		143	126	105	93	80	Norton ⁽²⁶⁾
	{ 28.0	6.5	8.5	10.5	12.4	14.0	15.7	Austin and Pierce ^(50a)
Silica.....	{ 29.0	7.0	8.9	10.3	11.7			
	{ 30.4	8.1	10.0	11.8	13.0	14.2	15.3	Norton ⁽²⁶⁾
Spinel.....	36.3	10.4	11.6	12.5	13.3	14.0	14.6	Norton ⁽²⁶⁾
Zirconia.....	29.5	10.4	11.3	12.2	13.0	13.7	14.3	Norton ⁽²⁶⁾

* *k* expressed as B.t.u. · hr.⁻¹ · ft.⁻² · in. · °F.⁻¹.

difficulties, the values for heavy refractories cannot be depended on closely.

Insulators.—Insulators are composed of a more or less refractory skeleton having a large proportion of pores. The basic material may be magnesium carbonate, asbestos, silica, clay, or glass fibers. The values of *k* for a number of typical materials are shown in Table 77. For data on any specific product, it is necessary to get in touch with the manufacturer or make an individual test of the material.

It will be noted that in general, the lighter the insulator the lower will be the value of *k* at low temperatures. There is a lower limit, however, as mineral wool, for example, below 5 lb.

TABLE 77. THERMAL CONDUCTIVITY OF INSULATING MATERIALS

TABLE 77. THERMAL CONDUCTIVITY OF INSULATING MATERIALS.

Type of insulation	Linear shrinkage, 5 hr. reheat, per cent at °F.	Density, lb. per cu. ft.	Mean thermal conductivity* at a mean temperature of					
			200°F.	400°F.	800°F.	1200°F.	1600°F.	2000°F. 2400°F.
Insulating firebrick:								
Kaolin base.....	1.00 at 2900	55			2.9	3.3	3.9	1.5 5.2
Kaolin base.....	1.00 at 2800	44			2.1	2.8	3.3	3.8 4.4
Kaolin base.....	3.10 at 2600	48		2.5	2.8	3.2	3.7	
Fireclay base.....	0.10 at 2300	26		0.8	1.0	1.3	1.5	
Insulating brick:								
Raw diatomaceous earth base.....	1.00 at 1100	33	0.7	0.8	0.9	1.0		
Calcined diatomaceous earth base.....	2.80 at 2300	13			1.4	1.6	2.0	
High-temperature block insulation:								
Diatomaceous earth base.....	3.10 at 1900	23	0.58	0.62	0.70	0.80		
Diatomaceous earth base.....	0.75 at 1600	18.5	0.55	0.67	0.80	0.95		
Vermiculite base.....	1.69 at 1600	22	0.42	0.56	0.81			
Mineral wool base.....		19	0.58	0.67	0.91	1.21		
Kaolin base.....								
Insulating blankets:								
Mineral-wool base.....	1000	8-12	0.38	0.52	0.78			
Mineral-wool base.....	800	8-12	0.35	0.51				
Glass-wool base.....	1000	3	0.31	0.36	0.57			
Plastic insulating cements:								
Diatomaceous base.....	1900	40	0.65	0.72	0.82	1.00		
Mineral-wool base.....	1200	24	0.67	0.75	0.93			
Vermiculite base.....	1500	15	0.75	0.83	1.10			
Asbestos base.....	1200	17	0.80	0.93	1.25			
85 per cent magnesia.....	600	15	0.49	0.55				

* k expressed as B.t.u. · hr.⁻¹ · ft.⁻² · in. · °F.⁻¹.

per cu. ft. density shows an increasing value of k . In general, material with the smallest pores has the slowest increase in conductivity with increasing temperature; but here again, much research is needed to develop a general theory of heat conduction in porous materials, although this has been considered by some writers.⁽³⁸⁾

5. Flow of Heat through Walls under Steady Conditions.

Computation of Heat Flow in a Simple Wall.—The flow of heat

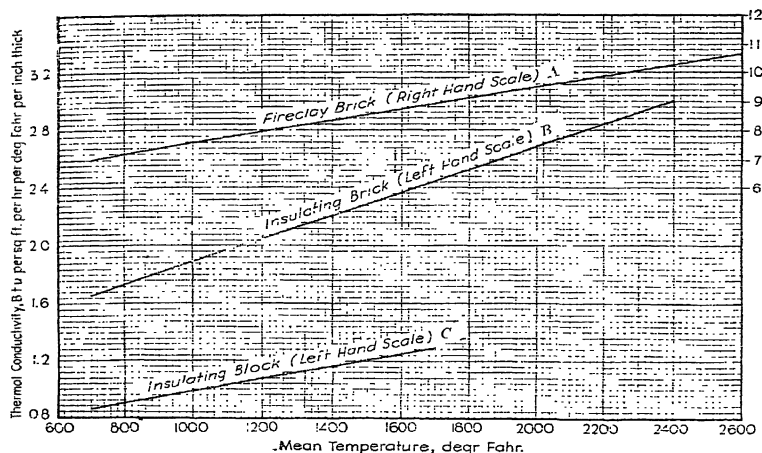


FIG. 307.—Average curves of thermal conductivity used in calculations. (From R. H. Heilman, A.S.T.M. Committee C-8 on Refractories.)

through simple walls is dependent on the thermal conductivity at the mean wall temperature and the temperature difference between the hot and cold face. Also it should be remembered that the quantity of heat passing through the wall must be equal to the heat leaving the wall. The latter is also dependent on the cold-face temperature and the velocity of the air outside the wall.

The calculation of the heat flow will be made clearer by a specific example. Assume a 9-in. refractory wall heated on the hot side to 2200°F. The outside air is 80°F. and not moving. The values of k for this particular refractory are given by curve A in Fig. 307. The quantity of heat lost from the outside of the wall, q_{rc} , is given by Heilman's curve in Fig. 308. We may

write from Eq. (1)

$$q = \frac{t_1 - t_n}{L/k} = \frac{2200 - t_n}{9/k} = q_{rc}$$

but as k varies with $(t_1 - t_n)/2$ and q_{rc} varies with t_n , the equation cannot be solved directly. Therefore, we must assume a

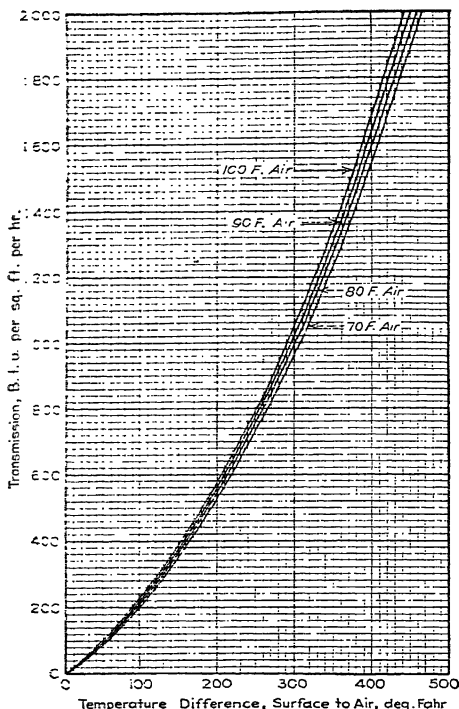


FIG. 30S.—Heat transmission from a vertical surface. (From R. H. Heilman, A.S.T.M. Committee C-8 on Refractories.)

mean temperature and an outside temperature. If q and q_{rc} were not equal, another and closer assumption of values is made until the required precision is reached. Assume $t_n = 300^\circ\text{F}$. and $k = 8.1$, then

$$q = \frac{2200 - 300}{9/8.1} = 1710 \quad q_{rc} = 620 \text{ from curve}$$

The cold face has been taken too low, so 500 will be taken for the next trial.

$$q = \frac{2200 - 500}{9/8.1} = 1720 \quad q_{rc} = 1530 \text{ from curve}$$

This gives a mean temperature of 1350°F.; hence, a more precise value of k from the curve is 8.2. Choosing a lower cold-face temperature of 480°F. gives

$$q = \frac{2200 - 480}{9/8.2} = 1570 \quad q_{rc} = 1590$$

which is sufficiently close.

Computation of Heat Flow in a Compound Wall.—In this case, the value of q is the same for each layer of the wall of unit area and equal to the heat leaving the cold face. As another example, a 9-in. firebrick wall with a 2400°F. hot face is backed up with 4.5 in. of insulating brick and 2 in. of insulating block. The air conditions are the same as before. From Eq. (2)

$$q = \frac{2400 - t_n}{(9/k_1) + (4.5/k_2) + 2/k_3} = q_r$$

As a first trial, assume $t_n = 280^\circ\text{F.}$ and k_1 , k_2 , and k_3 as 9.5, 2.0, and 0.9, respectively, from Fig. 307. Then

$$q = \frac{2400 - 280}{(9/9.5) + (4.5/2.0) + (2/0.9)} = \frac{2120}{0.95 + 2.25 + 2.23} = 390$$

$$q_{rc} = 545 \text{ from curve}$$

Next assume $t_n = 245$, then

$$q = 398 \quad q_{rc} = 417$$

which is sufficiently close for a first approximation.

Now from Eq. (3)

$$\begin{array}{rcl} t_1 - t_2 & = & 398 \times 0.95 = 375 \\ t_2 - t_3 & = & 398 \times 2.25 = 895 \\ t_3 - t_n & = & 398 \times 2.23 = 890 \\ t_1 - t_n & = & \underline{2160} \end{array}$$

The interface temperatures will be 2025 and 1130°F.; the mean temperatures of each layer will be 2212, 1577, and 685°F. Now go back to the conductivity curves and select more precise values of k , which will be respectively 9.90, 2.35, and 0.85. The heat flow is now worked out again, with $t_n = 245$.

$$q = \frac{2400 - 245}{(9/9.9) + (4.5/2.35) + (2/0.85)} = \frac{2155}{0.91 + 1.91 + 2.35} = \frac{2155}{5.17} = 417$$

which is the same as q_r . Now the temperature drops are recalculated:

$$\begin{aligned} t_1 - t_2 &= 417 \times 0.91 = 379 \\ t_2 - t_3 &= 417 \times 1.91 = 795 \\ t_3 - t_n &= 417 \times 2.35 = 981 \\ t_1 - t_n &= \frac{2155}{5.17} \end{aligned}$$

The interface temperatures will then be 2021 and 1226°F.

The mean temperatures will be 2210, 1623, and 612°F. Taking new values for k and t_n of 242°F.,

$$q = \frac{2400 - 242}{(9/9.9) + (4.5/2.39) + (2/0.81)} = \frac{2158}{0.91 + 1.88 + 2.47} = \frac{2158}{5.26} = 410$$

and $q_r = 410$ as closely as can be read.

The values of temperature drops are

$$\begin{aligned} t_1 - t_2 &= 410 \times 0.91 = 373 \\ t_2 - t_3 &= 410 \times 1.88 = 772 \\ t_3 - t_n &= 410 \times 2.47 = 1013 \\ t_1 - t_n &= \frac{2158}{5.26} \end{aligned}$$

Therefore the interface temperatures are 2027 and 1256°F., and the mean temperatures are 2213, 1641, and 627°F. By further trial, any degree of precision can be obtained, but the fourth trial here is sufficiently exact for ordinary purposes, as we do not know the conductivity values very accurately. Computing walls is a tedious process; but with experience, the initial selection of temperature will be fairly close to the final values. The heat flow and heat storage in a number of standard wall constructions are shown in Table 78.

6. Computation of Heat Flow in Cylinders. *Through Circular Structures.*—Although the same general method is used for determining heat flow through circular structures, the equation for heat flow through a plane wall cannot be applied to flow through a cylinder if an accurate result is desired. The reason for this may readily be understood when it is considered that the inside circumference of a cylinder is smaller than the outside circumference. Consequently, heat spreads out as it travels from the inside to the outside, and, conversely, it converges when the direction of flow is from the outside toward the inside.

Heat flow outward through a cylinder may be calculated by the following formulas:

1. For a wall of one material:

$$q = \frac{2\pi(t - t_n)}{(1/k_n) \ln (D_n/D)} \text{ B.t.u.}/(\text{lin.-ft.})(\text{hr.})$$

or

$$q = \frac{t - t_n}{(D_n/2k_n) \ln (D_n/D)} \text{ B.t.u.}/(\text{sq. ft.})(\text{hr.})$$

2. For a composite wall:

$$q = \frac{2\pi(t - t_n)}{\frac{1}{k_1} \ln \frac{D_1}{D} + \frac{1}{k_2} \ln \frac{D_2}{D_1} + \dots + \frac{1}{k_n} \ln \frac{D}{D_{(n-1)}}} \text{ B.t.u. (lin. ft.)(hr.)}$$

or

$$q = \frac{t - t_n}{\frac{D_n}{2k_1} \ln \frac{D_1}{D} + \frac{D_n}{2k_2} \ln \frac{D_2}{D_1} + \dots + \frac{D_n}{2k_n} \ln \frac{D_n}{D_{(n-1)}}} \text{ B.t.u. (sq. ft.)(hr.)}$$

where q = the quantity of heat, B.t.u. per hr.

t = the hot-face temperature

t_n = the cold-face or casing temperature

D = the inside diameter of cylinder, in.

D_1 = the outside diameter of inside lining material, in.

D_2 = the outside diameter of secondary lining material, in.

$D_{(n-1)}$ = the outside diameter of next to last lining material, in.

D_n = the outside diameter of outside lining material, in.

k_1 = the thermal conductivity of inside lining material

	11½	13½	15½	17½	19½	21½	23½	25½	27½	29½	31½	33½	35½	37½	39½	41½	43½	45½	47½	49½	51½	53½	55½	57½	59½	61½	63½	65½	67½	69½	71½	73½	75½	77½	79½	81½	83½	85½	87½	89½	91½	93½	95½	97½	99½	101½	103½	105½	107½	109½	111½	113½	115½	117½	119½	121½	123½	125½	127½	129½	131½	133½	135½	137½	139½	141½	143½	145½	147½	149½	151½	153½	155½	157½	159½	161½	163½	165½	167½	169½	171½	173½	175½	177½	179½	181½	183½	185½	187½	189½	191½	193½	195½	197½	199½	201½	203½	205½	207½	209½	211½	213½	215½	217½	219½	221½	223½	225½	227½	229½	231½	233½	235½	237½	239½	241½	243½	245½	247½	249½	251½	253½	255½	257½	259½	261½	263½	265½	267½	269½	271½	273½	275½	277½	279½	281½	283½	285½	287½	289½	291½	293½	295½	297½	299½	301½	303½	305½	307½	309½	311½	313½	315½	317½	319½	321½	323½	325½	327½	329½	331½	333½	335½	337½	339½	341½	343½	345½	347½	349½	351½	353½	355½	357½	359½	361½	363½	365½	367½	369½	371½	373½	375½	377½	379½	381½	383½	385½	387½	389½	391½	393½	395½	397½	399½	401½	403½	405½	407½	409½	411½	413½	415½	417½	419½	421½	423½	425½	427½	429½	431½	433½	435½	437½	439½	441½	443½	445½	447½	449½	451½	453½	455½	457½	459½	461½	463½	465½	467½	469½	471½	473½	475½	477½	479½	481½	483½	485½	487½	489½	491½	493½	495½	497½	499½	501½	503½	505½	507½	509½	511½	513½	515½	517½	519½	521½	523½	525½	527½	529½	531½	533½	535½	537½	539½	541½	543½	545½	547½	549½	551½	553½	555½	557½	559½	561½	563½	565½	567½	569½	571½	573½	575½	577½	579½	581½	583½	585½	587½	589½	591½	593½	595½	597½	599½	601½	603½	605½	607½	609½	611½	613½	615½	617½	619½	621½	623½	625½	627½	629½	631½	633½	635½	637½	639½	641½	643½	645½	647½	649½	651½	653½	655½	657½	659½	661½	663½	665½	667½	669½	671½	673½	675½	677½	679½	681½	683½	685½	687½	689½	691½	693½	695½	697½	699½	701½	703½	705½	707½	709½	711½	713½	715½	717½	719½	721½	723½	725½	727½	729½	731½	733½	735½	737½	739½	741½	743½	745½	747½	749½	751½	753½	755½	757½	759½	761½	763½	765½	767½	769½	771½	773½	775½	777½	779½	781½	783½	785½	787½	789½	791½	793½	795½	797½	799½	801½	803½	805½	807½	809½	811½	813½	815½	817½	819½	821½	823½	825½	827½	829½	831½	833½	835½	837½	839½	841½	843½	845½	847½	849½	851½	853½	855½	857½	859½	861½	863½	865½	867½	869½	871½	873½	875½	877½	879½	881½	883½	885½	887½	889½	891½	893½	895½	897½	899½	901½	903½	905½	907½	909½	911½	913½	915½	917½	919½	921½	923½	925½	927½	929½	931½	933½	935½	937½	939½	941½	943½	945½	947½	949½	951½	953½	955½	957½	959½	961½	963½	965½	967½	969½	971½	973½	975½	977½	979½	981½	983½	985½	987½	989½	991½	993½	995½	997½	999½	1001½	1003½	1005½	1007½	1009½	1011½	1013½	1015½	1017½	1019½	1021½	1023½	1025½	1027½	1029½	1031½	1033½	1035½	1037½	1039½	1041½	1043½	1045½	1047½	1049½	1051½	1053½	1055½	1057½	1059½	1061½	1063½	1065½	1067½	1069½	1071½	1073½	1075½	1077½	1079½	1081½	1083½	1085½	1087½	1089½	1091½	1093½	1095½	1097½	1099½	1101½	1103½	1105½	1107½	1109½	1111½	1113½	1115½	1117½	1119½	1121½	1123½	1125½	1127½	1129½	1131½	1133½	1135½	1137½	1139½	1141½	1143½	1145½	1147½	1149½	1151½	1153½	1155½	1157½	1159½	1161½	1163½	1165½	1167½	1169½	1171½	1173½	1175½	1177½	1179½	1181½	1183½	1185½	1187½	1189½	1191½	1193½	1195½	1197½	1199½	1201½	1203½	1205½	1207½	1209½	1211½	1213½	1215½	1217½	1219½	1221½	1223½	1225½	1227½	1229½	1231½	1233½	1235½	1237½	1239½	1241½	1243½	1245½	1247½	1249½	1251½	1253½	1255½	1257½	1259½	1261½	1263½	1265½	1267½	1269½	1271½	1273½	1275½	1277½	1279½	1281½	1283½	1285½	1287½	1289½	1291½	1293½	1295½	1297½	1299½	1301½	1303½	1305½	1307½	1309½	1311½	1313½	1315½	1317½	1319½	1321½	1323½	1325½	1327½	1329½	1331½	1333½	1335½	1337½	1339½	1341½	1343½	1345½	1347½	1349½	1351½	1353½	1355½	1357½	1359½	1361½	1363½	1365½	1367½	1369½	1371½	1373½	1375½	1377½	1379½	1381½	1383½	1385½	1387½	1389½	1391½	1393½	1395½	1397½	1399½	1401½	1403½	1405½	1407½	1409½	1411½	1413½	1415½	1417½	1419½	1421½	1423½	1425½	1427½	1429½	1431½	1433½	1435½	1437½	1439½	1441½	1443½	1445½	1447½	1449½	1451½	1453½	1455½	1457½	1459½	1461½	1463½	1465½	1467½	1469½	1471½	1473½	1475½	1477½	1479½	1481½	1483½	1485½	1487½	1489½	1491½	1493½	1495½	1497½	1499½	1501½	1503½	1505½	1507½	1509½	1511½	1513½	1515½	1517½	1519½	1521½	1523½	1525½	1527½	1529½	1531½	1533½	1535½	1537½	1539½	1541½	1543½	1545½	1547½	1549½	1551½	1553½	1555½	1557½	1559½	1561½	1563½	1565½	1567½	1569½	1571½	1573½	1575½	1577½	1579½	1581½	1583½	1585½	1587½	1589½	1591½	1593½	1595½	1597½	1599½	1601½	1603½	1605½	1607½	1609½	1611½	1613½	1615½	1617½	1619½	1621½	1623½	1625½	1627½	1629½	1631½	1633½	1635½	1637½	1639½	1641½	1643½	1645½	1647½	1649½	1651½	1653½	1655½	1657½	1659½	1661½	1663½	1665½	1667½	1669½	1671½	1673½	1675½	1677½	1679½	1681½	1683½	1685½	1687½	1689½	1691½	1693½	1695½	1697½	1699½	1701½	1703½	1705½	1707½	1709½	1711½	1713½	1715½	1717½	1719½	1721½	1723½	1725½	1727½	1729½	1731½	1733½	1735½	1737½	1739½	1741½	1743½	1745½	1747½	1749½	1751½	1753½	1755½	1757½	1759½	1761½	1763½	1765½	1767½	1769½	1771½	1773½	1775½	1777½	1779½	1781½	1783½	1785½	1787½	1789½	1791½	1793½	1795½	1797½	1799½	1801½	1803½	1805½	1807½	1809½	1811½	1813½	1815½	1817½	1819½	1821½	1823½	1825½	1827½	1829½	1831½	1833½	1835½	1837½	1839½	1841½	1843½	1845½	1847½	1849½	1851½	1853½	1855½	1857½	1859½	1861½	1863½	1865½	1867½	1869½	1871½	1873½	1875½	1877½	1879½	1881½	1883½	1885½	1887½	1889½	1891½	1893½	1895½	1897½	1899½	1901½	1903½	1905½	1907½	1909½	1911½	1913½	1915½	1917½	1919½	1921½	1923½	1925½	1927½	1929½	1931½	1933½	1935½	1937½	1939½	1941½	1943½	1945½	1947½	1949½	1951½	1953½	1955½	1957½	1959½	1961½	1963½	1965½	1967½	1969½	1971½	1973½	1975½	1977½	1979½	1981½	1983½	1985½	1987½	1989½	1991½	1993½	1995½	1997½	1999½	2001½	2003½	2005½	2007½	2009½	2011½	2013½	2015½	2017½	2019½	2021½	2023½	2025½	2027½	2029½	2031½	2033½	2035½	2037½	2039½	2041½	2043½	2045½	2047½	2049½	2051½	2053½	2055½	2057½	2059½	2061½	2063½	2065½	2067½	2069½	2071½	2073½	2075½	2077½	2079½	2081½	2083½	2085½	2087½	2089½	2091½	2093½	2095½	2097½	2099½	2101½	2103½	2105½	2107½	2109½	2111½	2113½	2115½	2117½	2119½	2121½	2123½	2125½	2127½	2129½	2131½	2133½	2135½	2137½	2139½	2141½	2143½	2145½	2147½	2149½	2151½	2153½	2155½	2157½	2159½	2161½	2163½	2165½	2167½	2169½	2171½	2173½	2175½	2177½	2179½	2181½	2183½	2185½	2187½	2189½	2191½	2193½	2195½	2197½	2199½	2201½	2203½	2205½	2207½	2209½	2211½	2213½	2215½	2217½	2219½	2221½	2223½	2225½	2227½	2229½	2231½	2233½	2235½	2237½	2239½	2241½	2243½	2245½	2247½	2249½	2251½	2253½	2255½	2257½	2259½	2261½	2263½	2265½	2267½	2269½	2271½	2273½	2275½	2277½	2279½	2281½	2283½	2285½	2287½	2289½	2291½	2293½	2295½	2297½	2299½	2301½	2303½	2305½	2307½	2309½	2311½	2313½	2315½	2317½	2319½	2321½	2323½	2325½	2327½	2329½	2331½	2333½	2335½	2337½	2339½	2341½	2343½	2345½	2347½	2349½	2351½	2353½	2355½	2357½	2359½	2361½	2363½	2365½	2367½	2369½	2371½	2373½	2375½	2377½	2379½	2381½	2383½	2385½	2387½	2389½	2391½	2393½	2395½	2397½	2399½	2401½	2403½	2405½	2407½	2409½	2411½	2413½	2415½	2417½	2419½	2421½	2423½	2425½	2427½	2429½	2431½	2433½	2435½	2437½	2439½	2441½	2443½	2445½	2447½	2449½	2451½	2453½	2455½	2457½	2459½	2461½	2463½	2465½	2467½	2469½	2471½	2473½	2475½	2477½	2479½	2481½	2483½	2485½	2487½	2489½	2491½	2493½	2495½	2497½	2499½	2501½	2503½	2505½	2507½	2509½	2511½	2513½	2515½	2517½	2519½	2521½	2523½	2525½	2527½	2529½	2531½	2533½	2535½	2537½	2539½	2541½	2543½	2545½	2547½	2549½	2551½	2553½	2555½	2557½	2559½	2561½	2563½	2565½	2567½	2569½	2571½	25
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[illegible]

16 = 1600°F, I/FB 20 = 2000°F, I/FB 23 = 2300°F, I/FB 26 = 2600°F, I/FB 28 = 2800°F, I/FB 30 = 3000°F, I/FB, HL = heat loss in B.t.u./sq. ft./hr.) Based on still-air temperature of 80°F. IIS = heat storage capacity in B.t.u. per sq. ft.

k_2 = the thermal conductivity of secondary lining material

k_n = the thermal conductivity of outside lining material

k_1 , k_2 and k_n are expressed in B.t.u. · hr.⁻¹ · ft.⁻² · in. · deg. F.⁻¹

Interface temperatures between various layers are expressed as

t_1 = the temperature at D_1 , deg. F.

t_2 = the temperature at D_2 , deg. F.

T_{n-1} = the temperature at $D_{(n-1)}$, deg. F.

For a case in which the flow of heat is from the outside of the cylinder toward the center, D would become the outside or largest diameter and D_n the inside or smallest diameter.

The preceding formulas involve the use of natural logarithms. If such a table is unavailable or inconvenient to use, common logarithms may be substituted and multiplied by 2.303.

7. Flow of Heat through Furnace Walls under Variable Conditions.—The temperature distribution in a simple or composite wall can be computed approximately for conditions of unsteady heat flow mathematically or graphically by the method of E. Schmidt. Such calculations require values of diffusivity for each material over the whole temperature range and, at best, are only approximate. For a discussion of this method, which requires too much space to treat here, reference should be made to Trinks⁽⁵⁰⁾ or Schack.^(40a) Composite walls require a very complicated set of calculations.

Practically, the problem can be solved quite readily by constructing a small section of the wall as the side or door of a furnace. Couples on the faces and between the layers will give the temperature distribution accurately. The value of q passing out from the wall can be estimated fairly closely from the outside temperature.

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CHAPTER XVIII

SIZES AND TOLERANCES

1. Standard Shapes.—A standard shape is a refractory brick other than a straight $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ -in. size which is generally stocked by all refractory manufacturers. Although all manufacturers do not agree as to what constitutes a standard shape, there are many universally accepted ones that may safely be specified in any design work.

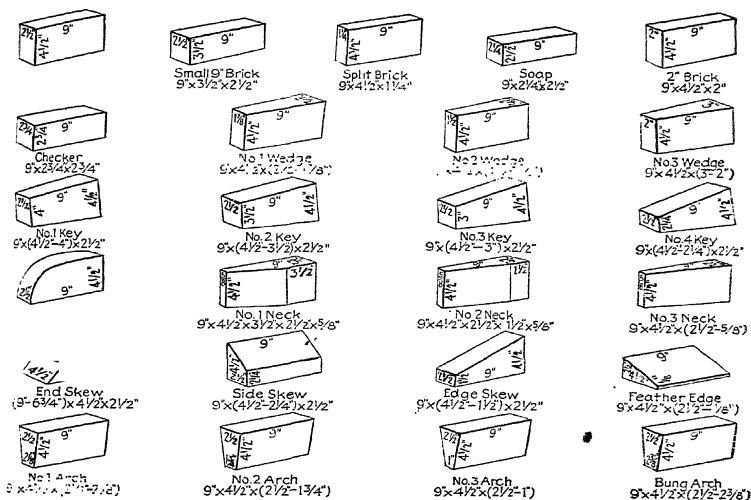


FIG. 309.—Standard shapes (9-in. series).

Standard shapes are used in all types of construction to save cutting straight brick, as illustrated in Chap. XXIV.

In Figs. 309 and 310 are given the sizes of the generally accepted standard firebrick shapes. Of course, many others are stocked as standard by individual companies, and these will be treated separately as special shapes.

The size tolerance on standard shapes and straight brick is given by the American Society for Testing Materials as ± 2 per cent, which covers both shrinkage and warpage on all dimensions over 4 in. On dimensions less than this, a tolerance of 3 per cent is specified. A.S.T.M. method C 154-41 is used in measuring.

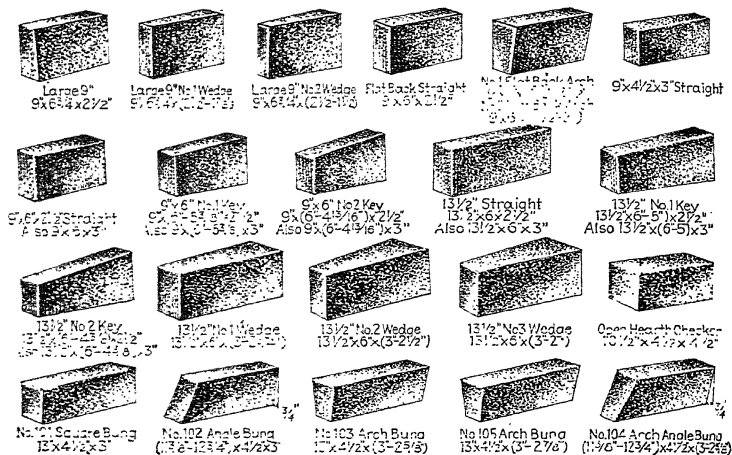


FIG. 310.—Standard shapes of firebrick (larger than 9 in.).

Warpage is measured by laying a straightedge along a concave diagonal and inserting a calibrated wedge under the straightedge at the center of the tile. The American Refractories Institute recommends that warpage should not exceed 1 per cent of the diagonal. ⁽¹³⁾

⁷ Silica standard shapes are approximately the same as firebrick shapes. Magnesite and chrome refractories can be called standard only in the simpler shapes of the 9-in. series. The manufacturer's catalogue should always be consulted, as shapes stocked by one company might not be stocked by another.

2. Special Shapes. *Glass-tank Blocks.*—Shapes that are used only for certain particular types of construction may be obtained from stock at times but are not generally available without ordering ahead. This class includes glass-tank blocks. Unfortunately there is little standardization of these blocks, but a few of the favorite sizes are listed in Table 79.

TABLE 79

Common Sizes of Flux Blocks for Continuous Tanks

12 × 18 × 24 in.	12 × 18 × 42 in.	12 × 24 × 36 in.
12 × 18 × 30 in.	12 × 18 × 48 in.	12 × 24 × 42 in.
12 × 18 × 36 in.	12 × 24 × 30 in.	12 × 24 × 48 in.

Common Sizes of Flux Blocks for Day Tanks

8 × 12 × 24 in.	8 × 18 × 24 in.	8 × 24 × 30 in.
8 × 12 × 30 in.	8 × 18 × 30 in.	8 × 24 × 36 in.
8 × 12 × 36 in.	8 × 18 × 36 in.	8 × 24 × 42 in.
	8 × 18 × 42 in.	

Glass-tank blocks, or flux blocks as they are usually termed, are generally made with more care than other large shapes. The clays are carefully blended and aged; the molding is carried out in such a way as to give a homogeneous structure; and the faces of the block are often ground accurately to dimensions. Besides the rectangular blocks, there are many special blocks used in tanks, such as the throat blocks.

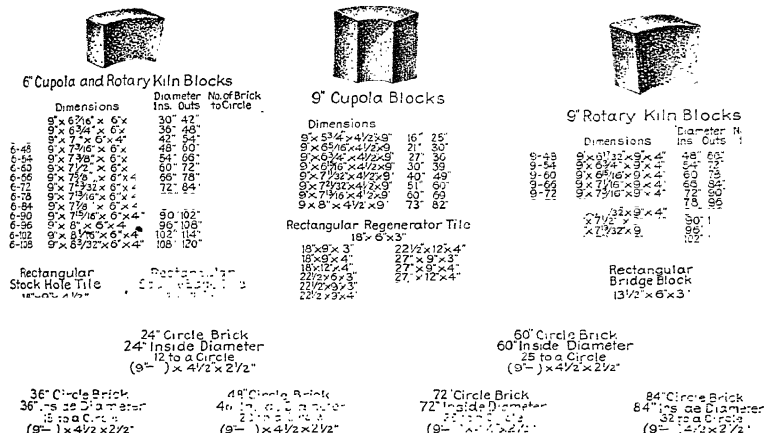


FIG. 311.—Shapes and sizes of radial blocks.

Cupola and Rotary-kiln Blocks.—These blocks are segments of a ring and are used to form a cylindrical lining. The common sizes are given in Fig. 311. Many manufacturers carry these blocks as standard shapes:

Cupola blocks are generally made of a dense fireclay, but rotary-kiln blocks are usually made of a high-alumina clay or

magnesite, as these materials seem to resist the slag action well and hold a good coating of clinker.

Tile.—Rectangular tile of fireclay may usually be obtained in the sizes shown in Table 80.

TABLE 80.—COMMON SIZES OF FIRECLAY TILE

$2 \times 9 \times 12$ in.	$3 \times 6 \times 18$ in.	$4 \times 9 \times 18$ in.
$2 \times 12 \times 12$ in.	$3 \times 6 \times 22\frac{1}{2}$ in.	$4 \times 9 \times 22\frac{1}{2}$ in.
$2 \times 12 \times 15$ in.	$3 \times 9 \times 18$ in.	$4 \times 9 \times 27$ in.
$2 \times 12 \times 18$ in.	$3 \times 12 \times 12$ in.	$4 \times 12 \times 18$ in.
$2 \times 12 \times 24$ in.		$4 \times 12 \times 22\frac{1}{2}$ in.
		$4 \times 12 \times 27$ in.
		$4 \times 12 \times 36$ in.
$6 \times 12 \times 36$ in.	$8 \times 18 \times 42$ in.	
$6 \times 12 \times 42$ in.	$8 \times 18 \times 48$ in.	
$6 \times 12 \times 48$ in.	$8 \times 18 \times 54$ in.	
$6 \times 18 \times 36$ in.	$8 \times 24 \times 42$ in.	
$6 \times 18 \times 42$ in.	$8 \times 24 \times 48$ in.	
$6 \times 18 \times 48$ in.	$8 \times 24 \times 54$ in.	
$6 \times 24 \times 42$ in.		
$6 \times 24 \times 48$ in.		

Checker Brick.—These generally are available in the following size:

$$10\frac{1}{2} \times 4\frac{1}{2} \times 4\frac{1}{2} \text{ in.}$$

Malleable Furnace Shapes.—Certain shapes are made especially for malleable-iron furnaces. They include

Bung arch,	$9 \times 4\frac{1}{2} \times (2\frac{1}{2} \text{ to } 2\frac{3}{8})$ in.
	$13\frac{1}{2} \times 4\frac{1}{2} \times (3 \text{ to } 2\frac{5}{8})$ in.
	$13\frac{1}{2} \times 4\frac{1}{2} \times (3 \text{ to } 2\frac{7}{8})$ in.
Square bung,	$13\frac{1}{2} \times 4\frac{1}{2} \times 3$ in.
Angle bung,	$(13\frac{1}{2} \text{ to } 12\frac{1}{8}) \times 4\frac{1}{2} \times 3$ in.
Tap-out block,	$9 \times 7\frac{1}{2} \times 7\frac{1}{2}$ in.

Lime-kiln Brick.—Some special lime-kiln brick are made by a few manufacturers, usually of silica or high-alumina material.

Hot-blast Stove Checker Brick.—A number of stove-brick shapes are made for particular types of structure. They are stocked by several manufacturers.

Coke-oven Shapes.—Shapes for making up rectangular and beehive ovens are more or less standardized by a number of manufacturers. Shapes for by-product ovens are also stocked, but the number of shapes is so large that they cannot well be listed here.

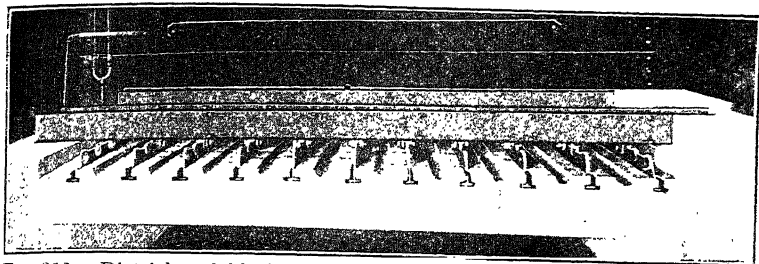


FIG. 312.—Dietrick arch blocks in a suspended arch. (Courtesy of M. H. Dietrick Company.)

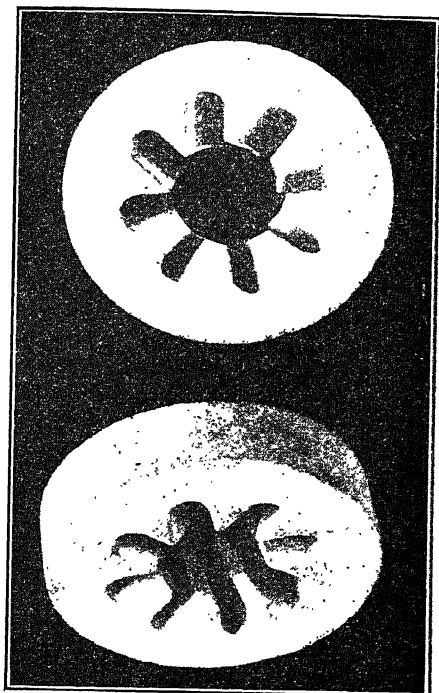


FIG. 313.—Burner tiles. (Courtesy of Babcock & Wilcox Company.)

Blocks for Suspended Arches.—There are a number of patented constructions for suspended arches requiring rather complicated blocks. One type of arch block is shown in Fig. 312. More details are given in Chap. XXIV.

Boiler Shapes.—There are a number of shapes used in stationary and locomotive boilers that are stocked by some manufacturers.

Other Special Shapes.—In addition to these, many special shapes are made for a particular installation, such as burner tile, impeller disks, hollow blocks, and feed-hole bricks. A special shape is shown in Fig. 313.

The Design of Special Shapes.—When designing a new furnace, it is often necessary to have special shapes made up. It should be remembered that special shapes, particularly when in small quantities, are relatively expensive and should be used only where they are necessary. A special shape should be made as simple as possible because complications increase the mold cost and do not permit as careful molding. Undercutting or thin projections should be avoided. It is also undesirable to specify thin slabs or bars because the loss by warping is apt to be large. In general, the shape should be as compact as possible and not exceed 24 in. in length. However, shapes can be made 48 in. long if necessary. A small shape generally has a better structure than a large one and is burned more evenly. Therefore the size of shapes should always be kept as small as practical. In designing special shapes to be used in conjunction with straight brick a good rule to follow is to make the vertical dimensions a multiple of $2\frac{9}{16}$ in. and the horizontal a multiple of $4\frac{9}{16}$ in. (the thickness and width of a straight brick plus one joint).

3. Kiln Furniture.—A considerable volume of refractories is used as kiln furniture, *i.e.*, supports and containers for ceramic ware while it is being fired. As the furniture must be heated and cooled with the ware, it is desirable to keep its mass down to a minimum in order to permit a more rapid heating and cooling cycle and increase the kiln efficiency. Because of the frequent temperature changes, the furniture must be able to resist spalling fairly well; and in many cases, it must be able to support a heavy load at high temperatures.

Saggers.—Saggers are refractory boxes for holding whiteware. They serve partly as a support and partly as muffles to protect

the ware from the kiln gases. The saggars are generally piled one on top of the other in bungs as shown in Fig. 314. A wadding of soft clay is placed between the saggars to make a tight joint. The ware is supported in the saggars in a variety of ways which we need not consider here.

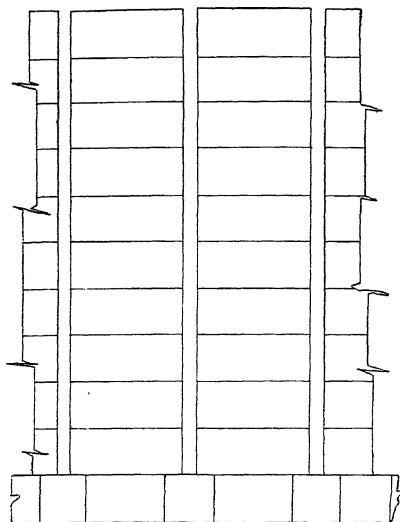


Fig. 314.—Saggars piled in bungs.

Saggars are made in a number of shapes and sizes, a few of which are shown in Fig. 315. However, there is no generally accepted standard. The wall thickness varies between $\frac{3}{8}$ and $\frac{7}{8}$ in. with an average of about $\frac{5}{8}$ in. The composition varies, but generally consists

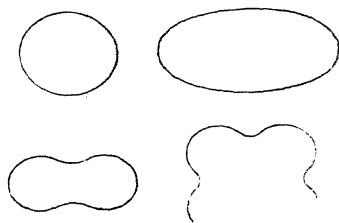


Fig. 315.—Common shapes of saggars.

of a grog (usually crushed saggars with the fines removed), a plastic clay to give strength, and a fire-clay to prevent too much vitrification. A good body should have a low coefficient of thermal expansion and an elastic structure, as explained in Chap. XIV.

The average life of a sagger is often no more than 25 burns. This short life is due to a poor body, nonhomogeneous molding, rough handling and, perhaps most important, lack of thorough preburning. As the sagger expense in the whiteware industry is a large item, a really superior sagger would be well worth while. Many manufacturers have experimented to some extent on saggars, and the U.S. Bureau of Standards has carried on a considerable investigation of this subject.

Another trouble with saggars is the separation of particles from the interior of the sagger, which may fall on the glazed ware and form serious defects. A sagger therefore must have a firm, smooth surface, and it is the usual practice to paint over the inside of the sagger with a wash of some low-vitrifying compound to form a sort of glaze.

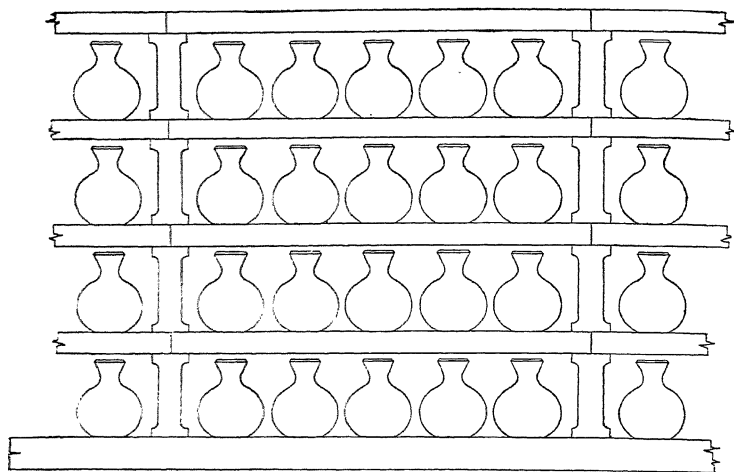


FIG. 316.—Setting tile where ware needs no protection from the atmosphere.

Saggars are made in a number of ways. Formerly they were all made by hand on a wooden form. This method requires considerable labor, but it was traditionally believed that first-class saggars could be made only by this method. Recently they have been made on a machine press, of which there are many kinds. Some excellent saggars are now made by casting a slip into a plaster mold.

Other materials have been used for saggars, such as silicon carbide, mullite, and zircon, but as yet they have not shown enough superiority over fireclay to warrant their increased cost.

Slabs and Posts.—In many cases, ware does not have to be protected from the kiln gases, so that supports as shown in Fig. 316 can be used. Generally the slabs are made of fireclay, fused alumina, or silicon carbide from $\frac{5}{8}$ to $2\frac{1}{2}$ in. thick, depending

on the size and load. Important advances have been made in open-setting kiln furniture in the last few years. Common sizes of setting slabs are given in Table 81.

TABLE 81.—REFRACTORY SLABS FOR OPEN-KILN SETTING

	Inches
Sanitary ware for straight T.K.....	$24 \times 36 \times 1\frac{1}{4}$
	$24 \times 36 \times 2\frac{1}{4}$
	$32 \times 25 \times 1\frac{1}{4}$
	$17 \times 25 \times 1\frac{1}{4}$
	$18 \times 24 \times \frac{3}{4}$
General ware and electrical porcelain for straight T.K.	$25\frac{1}{2} \times 21\frac{1}{2} \times 1$
	$20\frac{1}{2} \times 22\frac{1}{2} \times \frac{7}{8}$
Circular T.K.....	$32 \times 16\frac{1}{2} \times 18\frac{1}{2} \times 1$
	$32 \times 16\frac{1}{2} \times 18\frac{1}{2} \times \frac{3}{4}$
	$28 \times 16\frac{1}{2} \times 18\frac{1}{2} \times \frac{3}{4}$
	$28 \times 16\frac{1}{2} \times 18\frac{1}{2} \times \frac{1}{2}$
	$32 \times 16\frac{1}{2} \times 18\frac{1}{2} \times \frac{3}{4}$
	$32 \times 16\frac{1}{2} \times 18\frac{1}{2} \times \frac{1}{2}$

4. Muffles.—Muffles are generally used for enameled ware and for other articles when it is desired to keep them free from the furnace gases. Large muffles are constructed of sections of thin tile as shown in Fig. 317. The thickness is kept as low as possible, from $\frac{3}{4}$ to $1\frac{1}{4}$ in., in order to obtain the maximum rate of heat transfer. Sometimes each tile has its center recessed to an even thinner wall. The materials used for the muffle are fireclay, fused alumina, and silicon carbide. The high conductivity of the last two materials is of great advantage in this construction.

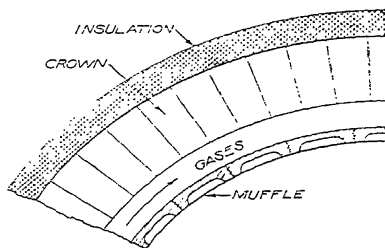


FIG. 317.—A large muffle.

Small muffles are used in many laboratory types of furnace. Fireclay, fused-alumina, and silicon carbide types can be obtained in many sizes. Small muffles of fused silica are available but cannot be used at high temperatures. A few of the common sizes of fireclay muffles are listed in Table 82.

5. Retorts.—Fireclay retorts for gas manufacture are from 7 to 10 ft. long and about 18 in. wide. The wall thickness is $2\frac{1}{2}$ to

3 in. in order to withstand the load. Since carbon closes up the pores when it is in use, the structure need not be dense but should be able to resist spalling.

TABLE 82.—COMMON SIZES OF FIRECLAY MUFFLES

Length, in.	Width	Height
7	3	2¼
8	4¾	3
10½	5¼	3⅞
12	6	4
12	8	5
15	9	5¾
16	10	5½
18	12¼	7¾
19	10½	6½

The body is usually made of about equal parts of plastic clay and grog. As in the case of saggers, the fine particles of the grog are removed. The retorts are usually hand-molded on to a form, but pressed retorts have been used. The finished retorts are

TABLE 83.—COMMON SIZES OF CLAY CRUCIBLES

Size	Height, inches	Diameter at top, inches
G	5⅝	3⅝
H	5⅞	3¾
I	6	4
J	6⅝	4⅝
K	7¼	4¾
L	8	5¼
M	8¼	5¾
N	9⅝	6½
O	10	7
P	11	7¾
Q	12	8¼
R	13	9⅝

burned in a vertical position in a firebrick kiln, and sometimes they are glazed. The more modern continuous retorts are vertical with a height of 40 to 50 ft. They are made up from silica shapes as shown in Fig. 318. A strong, dense structure is desired

to prevent the lining from coming off as a result of carbon deposited in the pores.

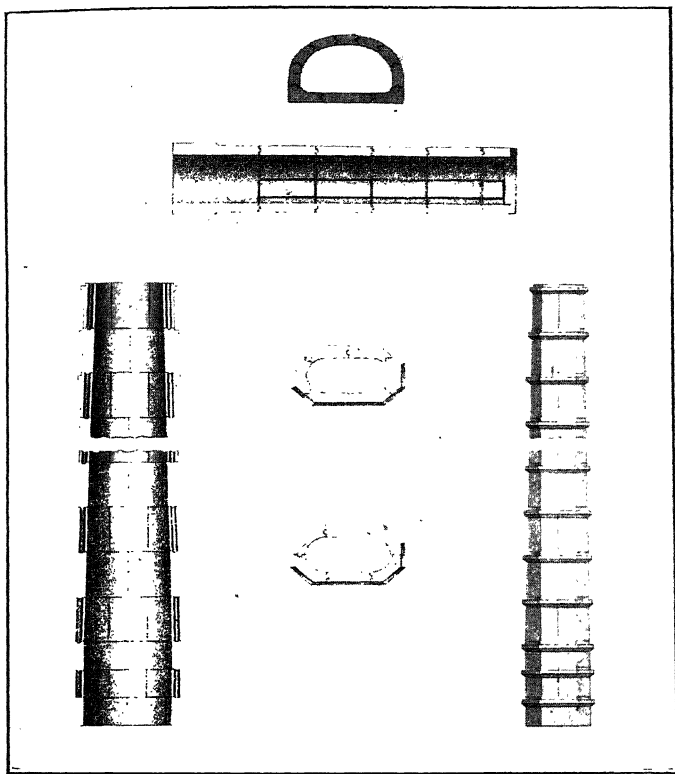


FIG. 318.—Silica retorts for gas production. (Courtesy of Harbison-Walker Refractories Company.)

6. Crucibles.—Crucibles are made of a great variety of refractory materials and in many shapes and sizes. It is, of course, impossible to list all of them here, but a few common sizes will be described.

Clay Crucibles.—Clay crucibles are made from fireclay and grog. The small ones are pressed, and the large ones made on a

jigger or flower-pot machine. The clay crucibles are generally used in small sizes for assaying, roasting, and low-temperature melting. Common shapes are shown in Fig. 319.

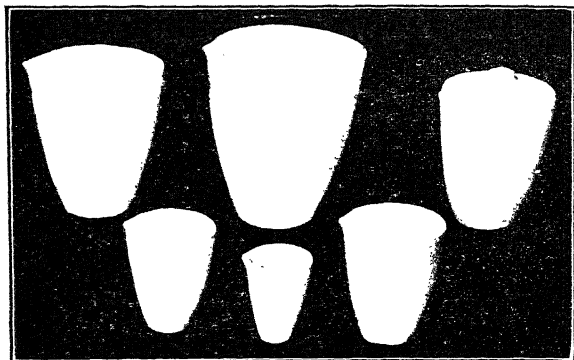


FIG. 319.—Common shape for clay crucibles. (Courtesy of Denver Fire Clay Company.)

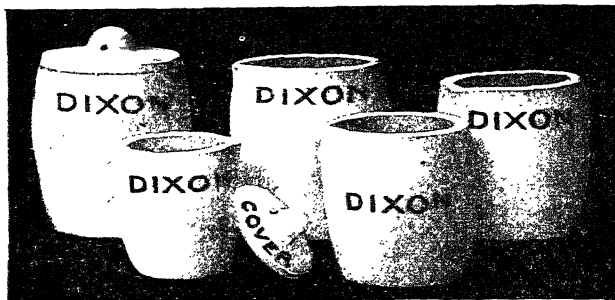


FIG. 320.—Shapes of graphite crucibles. (Courtesy of Joseph Dixon Crucible Company.)

The usual sizes of this clay crucible (Denver Fire Clay Company) are shown in Table 83.

Graphite Crucibles.—Graphite crucibles are extensively used for metal melting. The graphite increases the thermal conductivity and gives a strong body at high temperatures. These crucibles are made of a mixture of plastic fireclay and flake graphite. The amount of graphite varies between 6 and 50 per cent. The clay and graphite are thoroughly mixed in a wet pan

or pug mill and aged. The crucibles are formed on a jigger in the same manner as fireclay crucibles. The shape found most suitable for this type of crucible is shown in Fig. 320. A large number of standard sizes are available as given in Table 84 (Dixon).

TABLE 84.—COMMON SIZES OF GRAPHITE CRUCIBLES

Number (Dixon)	Outside	Outside
	diameter, in.	height, in.
0	1½	2
00	1⅞	2⅞
000	1⅞	2½
0000	2⅞	3
1	3⅞	3⅞
2	3¾	4½
3	4¼	5¼
4	4⅞	5⅞
5	4⅞	6
6	5¼	6¼
7	5½	6¾
8	5¾	7¼
10	6	8
14	6¾	8½
18	7¾	9¾
20	7¾	10¼
	up to	up to
400	19½	24¾

7. Glass Pots.—Glass pots are made of a suitable mixture of clays and grog. Before the First World War, most of the American manufacturers imported their glass-pot clays. Since then, domestic clays have been used successfully in nearly all cases. As a result mainly of the work of the U.S. Bureau of Standards the old hand-molded pots have been largely superseded by cast pots.

Apparently there are no generally accepted standards of size for pots, but covered pots are often 45 × 58 × 52 in. or 46 × 60 × 52 in. in width, length, and height, respectively. A typical covered pot is shown in Fig. 321.

8. Refractory Porcelain.—Refractory porcelain is used mainly for laboratory ware, spark plugs, and pyrometer protection tubes. It must have a high softening point, a dense structure, and a resistance as high as possible to spalling.

The high-mullite porcelains, sometimes made from calcined sillimanite or kyanite, undoubtedly give the best results from the point of view of strength at high temperatures and resistance

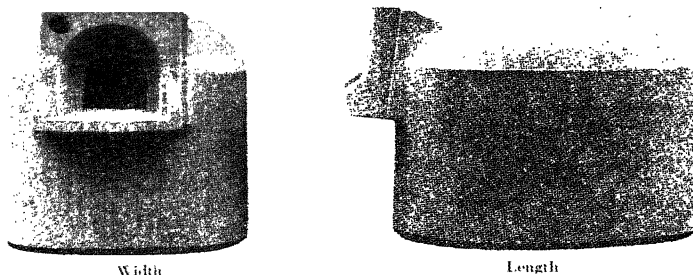


FIG. 321.—Covered glass melting pot. (Courtesy of Findlay Clay Products Company.)

to temperature changes. However, they require high firing, preferably up to 1650°C. (3000°F.).

TABLE 85.—COMMON SIZES OF REFRACTORY PORCELAIN TUBING

Type	Outside diameter, in.	Hole diameter, in.	Length, in.
Insulating tubing, 2-hole.	$\frac{1}{4}$	$\frac{1}{32}$	1-18
		$\frac{3}{64}$	1-48
		$\frac{1}{16}$	1-60
Insulating tubing, 1-hole.		$\frac{1}{16}$	1-12
		$\frac{1}{8}$	1-18
		$\frac{1}{4}$	1-48
Insulating tubing, 4-hole....	$\left\{ \begin{array}{l} \frac{3}{16} \\ \frac{5}{16} \end{array} \right.$	$\frac{3}{64}$	1-36
		$\frac{1}{16}$	1-48
Protection tubes, closed end.	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{4} \end{array} \right.$	$\frac{1}{8}$	6-18
		$\frac{9}{16}$	6-48

Little need be said about the forming and burning of refractory porcelain, as the procedure differs slightly from ordinary white-ware manufacture. The casting process is generally preferred for thin-walled objects. To prevent warping, tubes are hung from their upper ends while being burned.

It is necessary to glaze some high-temperature porcelains to prevent passage of gases. Perhaps the most complete study of high-temperature glazes is that by Sortwell.⁽³⁾

Refractory porcelain can be obtained in a large variety of sizes, glazed or unglazed. In Table 85 are shown some common sizes. Lengths up to 6 ft. can usually be obtained.

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CHAPTER XIX

MISCELLANEOUS PROPERTIES OF REFRACTORIES

A number of the less important properties of refractories and methods of test, which have not been included in the preceding chapters, are assembled here.

1. Measurement of Particle Size. Screen Analysis.—The determination of the particle-size distribution in a granular material is of considerable importance in ceramic work. For materials coarser than 150 to 300 mesh, screens are used to separate the material into any desired number of grades; but for the finer materials, air- or water-separation methods are most satisfactory.

The United States standard series of sieves is based upon a 1-mm. opening, the larger and smaller screens varying as $\sqrt{2}$, or 1.414. The characteristics of this series of screens are given in Table 86 on page 585.

The Tyler screens are more commonly used. They have as a basis a 200-mesh screen with an opening of 0.0029 in., and the sizes of opening also vary as the $\sqrt{2}$. The intermediate sizes are available to give closer spacing. In Table 87 on page 586 are given the characteristics of this series.

A sample to be screened should be completely dry, and the lumps broken up. It can then be passed through any required number of screens in series. Care must be taken, however, to shake the screens long enough to pass all undersized material through. A convenient piece of apparatus for making screen analyses is shown in Fig. 322. In some cases, wet screening is used, for example, to separate clay from grog.

A convenient method to make an analysis is to weigh out a sample of, say, 100 g. In obtaining this sample, the greatest care is necessary to ensure that it is representative. The sample is then passed through the desired screens, and the amount remaining on each screen is weighed. This weight in grams will give

the percentage directly. A typical analysis is shown in Table 88 on page 587.

TABLE 86.—UNITED STATES STANDARD SIEVE SERIES

Mesher per lineal inch	Sieve number	Sieve open- ing, inches	Sieve opening, millimeters	Wire diameter, inches	Wire diameter, millimeters
2.58	2½	0.315	8.00	0.073	1.85
3.03	3	0.265	6.73	0.065	1.65
3.57	3½	0.223	5.66	0.057	1.45
4.22	4	0.187	4.76	0.050	1.27
4.98	5	0.157	4.00	0.044	1.12
5.81	6	0.132	3.36	0.040	1.02
6.80	7	0.111	2.83	0.036	0.92
7.89	8	0.0937	2.38	0.0331	0.84
9.21	10	0.0787	2.00	0.0299	0.76
10.72	12	0.0661	1.68	0.0272	0.69
12.58	14	0.0555	1.41	0.0240	0.61
14.66	16	0.0469	1.19	0.0213	0.54
17.15	18	0.0394	1.00	0.0189	0.48
20.16	20	0.0331	0.84	0.0165	0.42
23.47	25	0.0280	0.71	0.0146	0.37
27.62	30	0.0232	0.59	0.0130	0.33
32.15	35	0.0197	0.50	0.0114	0.29
38.02	40	0.0165	0.42	0.0098	0.25
44.44	45	0.0138	0.35	0.0087	0.22
52.36	50	0.0117	0.297	0.0074	0.188
61.93	60	0.0098	0.250	0.0064	0.162
72.46	70	0.0083	0.210	0.0055	0.140
85.47	80	0.0070	0.177	0.0047	0.119
101.01	100	0.0059	0.149	0.0040	0.102
120.48	120	0.0049	0.125	0.0034	0.086
142.86	140	0.0041	0.105	0.0029	0.074
166.67	170	0.0035	0.088	0.0025	0.063
200.00	200	0.0029	0.074	0.0021	0.053
238.10	230	0.0024	0.062	0.0018	0.046
270.26	270	0.0021	0.053	0.0016	0.041
323.00	325	0.0017	0.044	0.0014	0.036

* There are a number of methods of plotting the results of a screen analysis. The fraction of each particular size of particle may be plotted on a frequency curve, as in Fig. 323, or the cumulative percentage may be plotted on logarithmic paper as is often done when using the Tyler screens (Fig. 324). Many

problem. The extensive work on fine grinding by Martin⁽⁹⁾ and others deserves careful study.

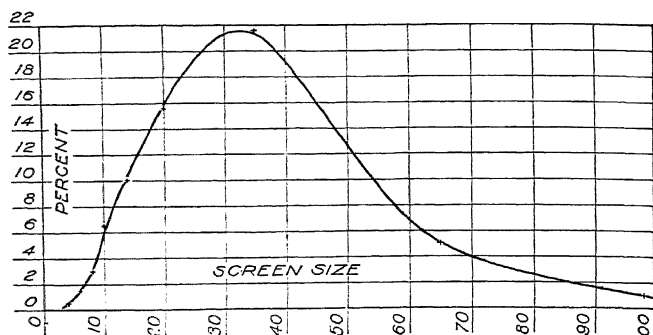


FIG. 323.—The result of a screen analysis. The fraction of each particle size plotted as a frequency curve.

Settling Methods.—In order to determine the particle-size distribution in a finely divided material such as a clay, the settling

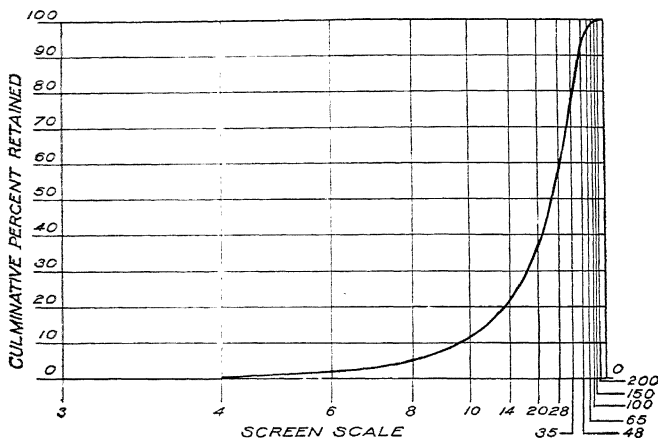


FIG. 324.—Result of a screen analysis.

rate of the particles in water is found to be their most useful property. Using Stokes' law, which states that a sphere of

diameter D will fall at a velocity V in a liquid of viscosity η when the density of the particle is S_1 and of the liquid S_2 , the diameter is found by

$$D = \frac{18\eta\bar{V}}{(S_1 - S_2)g}$$

in c.g.s. units.

It might be thought that the irregular or platelike particles would settle at a different rate from equivalent spheres; but with the exception of extreme plates such as are found in mica, Stokes' law is found to hold down to 1μ diameter and probably lower. The work of Wadell⁽¹⁹⁾ and Norton and Speil⁽²⁰⁾ confirm this.

One of the most important factors in this measurement is the complete dispersion of the particles in water. If they are flocculated to any extent, the results will be greatly in error. In the case of clays, considerable agitation is needed to break up clumps in addition to a deflocculating agent such as silicate of soda, sodium pyrophosphate, sodium carbonate, or Daxad. The state of dispersion should be checked with the microscope before the settling test.

When the particles are below 1μ in diameter, the settling rate becomes so slow that it must be accelerated by centrifugal force. As most of the particles in a clay are within this region, a special centrifuge (Fig. 325) has been developed recently for measurements down to 0.05μ . The amount of suspended material at any one time is determined by the specific gravity of the suspension as measured by a special hydrometer bulb. The pipette method⁽²¹⁾ of drawing off a small volume of suspension and drying down to find the suspended matter is slightly more precise than the hydrometer but more time consuming.

The standard test method used in the Ceramic Laboratory at the Massachusetts Institute of Technology is given below as taken from the *Journal of the American Ceramic Society*.⁽²⁰⁾

A 13-g. sample of the clay is shaken in 300 cc. of distilled water to which have been added 0.13 g. (1 per cent) of Daxad No. 23 (Dewey & Almy Chemical Co.). This is put through a hand homogenizer (Central Scientific Co., No. 70180), and transferred to a quart fruit jar. The jar is attached to a ball-mill frame and tumbled end over end at 60 r.p.m. for 5 days.

The sample is then transferred to the glass container, used in the centrifuge, and diluted to exactly 650 cc. A 1,000-cc. graduate is filled

are eliminated, because the value sought is the difference in specific gravity between the two and not the actual value of the specific gravity of the suspension. Temperature readings, precise to within $\pm 0.2^{\circ}\text{C}.$, are taken in each container for every test point, and the temperature is kept as constant as possible during a run. The hydrometer, when not in actual use, is wiped off and placed in the graduate containing the clear Daxad solution. The times at which the specific gravity should be read were determined arbitrarily to divide the region between 50 and 0.1μ into 20 approximately equal divisions when the data are plotted on semilogarithmic paper. Table 89 gives these time intervals, speed of

TABLE 89

Time interval	Speed, r.p.m.	Total equivalent time of gravity settling
Minutes:		Minutes:
1	Stationary	1
2	Stationary	3
2	Stationary	5
5	Stationary	10
10	Stationary	20
10	Stationary	30
30	Stationary	60
Hours:		Hours:
1	Stationary	2
1.5	Stationary	3.5
2.5	Stationary	6
Minutes:		
30	125	10.3
15	200	15.8
30	200	27
30	300	52
30	400	95
30	500	164
30	550	247
Hours:		
1.25	600	493
1.75	600	835
3	600	1,420
3.5	600	2,110
4.5	600	2,980
8	600	4,550

rotation, and the total elapsed time of equivalent gravity settling, based on an effective centrifuge radius of 49 centimeters.

In using the centrifuge, the elapsed time was taken between starting the centrifuge and shutting off the current to the motor. The acceleration and deceleration were rapid enough so that this approximate procedure was justified. The starting and stopping, however, must not be so sudden as to cause swirling of the suspension. In the tests carried out, the first day's run extended through 493 hr. so that any short interval of gravity settling after that time was practically negligible.

To change the data obtained from the sedimentation run into a distribution curve, the particle size or equivalent spherical diameter corresponding to each reading must be determined, as well as the percentage of material finer than this size. Using Stokes' law, the size which has settled to the center of the hydrometer bulb is easily obtained from the Casagrande nomographic chart.* It is necessary to calibrate only the distance-settled scale of the chart against the specific-gravity scale of the particular hydrometer used. Directions for this and also a key to the chart are given on the chart itself.

In using this distance-settled scale, a small meniscus correction (about 0.0003) must be added to the hydrometer reading, inasmuch as the actual distance settled is from the surface of the suspension (not the top of the meniscus) to the center of volume of the bulb. The value used on the temperature scale of the chart, which corrects for the temperature effect on the viscosity of water, should be the average over the test period up to the time of that reading.

For effective settling periods of more than 50 hr., better accuracy can be obtained with the chart by taking advantage of the fact that the size is given by the equation

$$D = kt^{-1/2}$$

where D = the diameter

t = the time

Thus the equivalent time is divided by a factor of 100 and, using this new time value, the size obtained from the chart is divided by ten to give the correct value. The reason for this step is to avoid large slopes between corresponding points on adjacent scales, a condition which decreases the accuracy of values obtained from the chart.

To determine the percentage of material finer than any given size, the following equation is used:

$$\text{W per cent} = \frac{S}{S-1} \times \frac{100}{C} (R-d) \times 10^3$$

* These charts may be obtained from Julius Springer in Berlin, or from the Soil Mechanics Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

where S = the specific gravity of suspended material.

C = the concentration of suspended matter, g. per l.

$R - d$ = the difference in specific gravity between suspension and corresponding standard reading at same temperature

The specific gravity of the clay can be obtained in a pycnometer bottle but runs close to 2.58 for kaolinite types of clays. To make this method clearer, an actual example is worked out in Table 90.

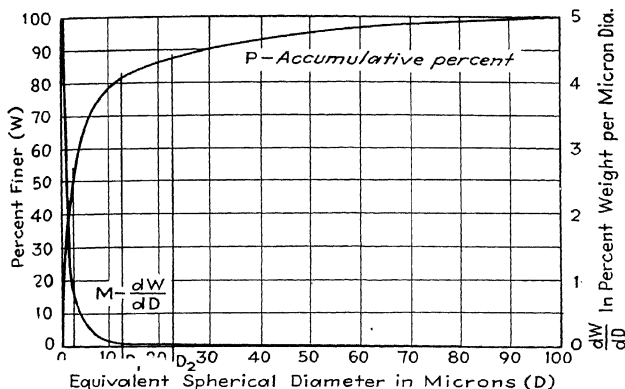


FIG. 326.—Size distribution for a typical clay plotted with linear coordinates. (*J. Am. Ceram. Soc.*)

The graphical representation of the results of a size analysis is generally carried out by plotting the weight per cent, W , finer than a given size as ordinates against that size, D , as abscissas. This method is shown in curve P of Fig. 326. A better picture of the distribution, however, can be obtained by plotting the function dW/dD against D as in curve M . This curve represents the slope of P and the area under it between any sizes D_1 and D_2 will be

$$\int y dx = \int_{D_2}^{D_1} \frac{dW}{dD} dD = \int_{W_{D_2}}^{W_{D_1}} dW = W_{D_1} - W_{D_2}$$

Therefore the weight of particles between D_1 and D_2 in Fig. 326 is equal to

$$\text{Total weight of sample} \times \frac{\text{area between } D_1 \text{ and } D_2}{\text{total area under } M}$$

For example, the line at 50 per cent W cuts the P curve at 2.3μ , through which a vertical line divides the area under M into two equal parts.

TABLE 90

Time	Centrifuge speed, r.p.m.	Acceleration × gravity	Equivalent settling time	Temperature, °C.	Reading R	Blank d	$R + C$	Size, microns	$(R - d) \times 10^3$	Per cent
			Minutes							
9.12	0	1.0	1	24.2	1.0106	0.9996	1.0109	29.0	11.0	91.7
9.13	0	1.0	3		1.0103		1.0106	17.2	10.7	88.8
9.15	0	1.0	5		1.0097	0.9996	1.0100	13.8	10.1	84.2
9.17	0	1.0	10		1.0092		1.0095	10.0	9.6	80.0
9.22	0	1.0	20	24.2	1.0084	0.9995	1.0087	7.4	8.8	73.0
9.32	0	1.0	30		1.0078	0.9995	1.0081	6.15	8.2	68.5
9.42	0	1.0	Hours							
10.12	0	1.0	1	24.5	1.0070	0.9995	1.0073	4.5	7.5	62.5
11.12	0	1.0	2	24.4	1.0060	0.9995	1.0063	3.3	6.5	54.4
12.42	0	1.0	3.5	23.9	1.0054	0.9997	1.0057	2.5	5.7	47.5
3.42	0	1.0	6.5	23.7	1.0048	0.9998	1.0051	1.92	5.0	41.9
3.49-4.16	125	8.6	10.3	24.2	1.0043	0.9997	1.0046	1.54	4.6	38.6
4.20-4.44	200	22.0	15.8	24.5	1.0039	0.9995	1.0042	1.25	4.4	36.6
5.00-5.30	200	22.0	26.8	24.1	1.0030	0.9996	1.0033	1.00	3.3	27.8
5.40-6.10	300	49.5	51.5	23.8	1.0023	0.9997	1.0026	0.73	2.6	21.6
6.19-6.49	400	88.0	95.5	24.9	1.0015	0.9993	1.0018	0.56	1.9	15.8
6.58-7.28	500	137.0	164	25.7	1.0003	0.9991	1.0006	0.42	1.2	10.4
7.30-8.09	550	166.0	247	25.7	1.0000	0.9991	1.0003	0.35	0.9	7.6
11.10-12.31	600	196.0	492	26.3	0.9994	0.9990	0.9997	0.25	0.4	3.6
1.00-2.45	600	196.0	834	27.1	0.9990	0.9988	0.9993	0.19	0.2	1.7
3.00-6.00	600	196.0	1422	28.0	0.9986	0.9985	0.9989	0.145	0.1	0.8
9.00-12.30	600	196.0	2107	28.1	0.9986	0.9986	0.9989	0.12	0.0	0.0
1.00-5.00	600	196.0	2990	27.7	0.9988	0.9988	0.9991	0.10	0.0	0.0

The distribution curve in Fig. 326 brings out strikingly the fact that clays have a large proportion of the particles in a very narrow range of sizes. The curve, however, is so crowded into the fine end that little precision is possible in reading the plot in this range. For this reason, it has been found better to plot the same data on semilog paper as in Fig. 327. Here the characteristics of the distribution in the fine fractions are brought out clearly, but the areas under the distribution curve have to be corrected for the scale, if they are used quantitatively. As in Fig. 326, the line passing through 50 per cent of W cuts the P curve at

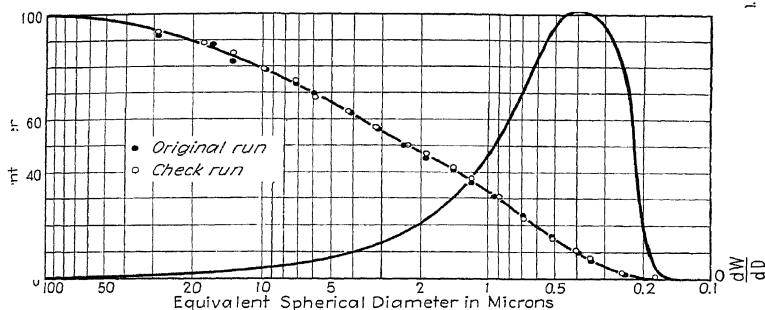


FIG. 327.—Size distribution for a typical clay plotted on semilogarithmic paper. (*J. Am. Ceram. Soc.*)

2.3μ and divides the plotted area under M into two equal parts. The actual area on the diagram, however, is quite different on the two sides of the line. The experimental points on the P curve show the consistency of the observations.

Other Methods.—Elutriation with either water or air as a medium may be used for the measurement of particle size, but this method is more useful for producing definite size fractions.

The microscope allows direct measurement of the particle sizes with a calibrated eyepiece. The lower limit, however, is about 1μ , but certain problems can well be handled by this method.

For finer sizes, the newly developed electron microscope gives us the only direct means of particle size measurement down to less than 0.1μ (see Fig. 40, Chap. V).

The X-ray diffraction pattern allows the calculation of particle sizes from 0.05μ and less by the line broadening that occurs with small particles. This method may also be used to measure the size of crystals in a lump of refractory.

A number of other methods have been used but are of minor importance in ceramics.

Interpretation of Particle Size.—The mean diameter of a single particle is clear when considering a sphere or cube where the diameter or edge respectively are definite measures. In the case of a parallelepiped with sides a , b , and c , we can express four mean diameters as follows:

$$dm = \frac{a + b + c}{3} \quad (\text{Statistical})$$

$$dm = \sqrt{\frac{2ab + 2ac + 2bc}{6}} \quad (\text{Side of a cube of equal area})$$

$$dm = \sqrt[3]{abc} \quad (\text{Side of a cube of equal volume})$$

$$dm = \frac{3abc}{ab + ac + bc} \quad (\text{Harmonic mean relating surface to volume})$$

For platelike particles the various dm 's vary a great deal, so the type of mean diameter should always be specified. The spherical mean diameter is usually taken as the diameter of a sphere settling at the same rate as the given particle.

When considering an evenly graded series of particles, the following mean diameters for the series may be written

$$d_{ms} = \frac{\sum nd}{\sum n} = \frac{1}{2} \frac{d_1^2 - d_2^2}{d_1 - d_2} = \frac{1}{2} (d_1 + d_2) \quad (\text{Statistical mean})$$

$$d_{mr} = \frac{\sum nd^2}{\sum nd} = \frac{2}{3} \frac{d_1^3 - d_2^3}{d_1^2 - d_2^2} \quad (\text{Length mean})$$

$$d_{ma} = \frac{\sum nd^3}{\sum nd^2} = \frac{3}{4} \frac{d_1^4 - d_2^4}{d_1^3 - d_2^3} \quad (\text{Area mean})$$

$$d_{mv} = \frac{\sum nd^4}{\sum nd^3} = \frac{4}{5} \frac{d_1^5 - d_2^5}{d_1^4 - d_2^4} \quad (\text{Volume mean})$$

where n = the total number of particles

d_1 = the smallest diameter in the series

d_2 = the largest diameter in the series

The so-called "Mellor mean" is often used

$$dm = \sqrt[3]{\frac{(d_1 + d_2)(d_1^2 + d_2^2)}{4}}$$

but does not seem to be based on any experimental evidence.

To illustrate the use of the various mean diameters, the following example based on an actual microscopic count by Perrott⁽⁸⁾ on an evenly graded series of particles is given in Table 91 below.

TABLE 91

Fraction diameter, microns.....	60	50	40	30	20	10	6	2
No. of particles.....	87	100	156	660	1,750	6,200	25,600	155,000
Percentage of total based on:								
Number $\frac{n}{\Sigma n}$	0.05	0.05	0.1	0.3	0.9	3.3	13.5	81.8
Length $\frac{nd}{\Sigma nd}$	0.9	0.9	1.1	3.5	6.1	10.9	22.4	54.3
Area $\frac{nd^2}{\Sigma nd^2}$	7.8	6.3	6.3	14.9	17.6	15.5	16.1	15.6
Volume $\frac{nd^3}{\Sigma nd^3}$	22.5	14.9	11.9	21.3	16.7	7.4	3.8	1.5

Calculating the mean diameter for the whole series gives

$$d_{ms} = \sum \left(\frac{n}{\Sigma n} \cdot d \right) = \frac{\Sigma nd}{\Sigma n} = 3.0\mu$$

$$d_{me} = \sum \left(\frac{nd}{\Sigma nd} \cdot d \right) = \frac{\Sigma nd^2}{\Sigma nd} = 7.0\mu$$

$$d_{ma} = \sum \left(\frac{nd^2}{\Sigma nd^2} \cdot d \right) = \frac{\Sigma nd^3}{\Sigma nd^2} = 21.0\mu$$

$$d_{mv} = \sum \left(\frac{nd^3}{\Sigma nd^3} \cdot d \right) = \frac{\Sigma nd^4}{\Sigma nd^3} = 36.4\mu$$

The physical significance of these values can be visualized by assuming that all the particles in the sample were laid out in a line, each particle touching the next and each being smaller than the one preceding it. If the particle in this line was selected that had equal numbers of particles above and below it, its diameter would be 3.0μ . On the other hand, if a particle were selected exactly in the center of the line, it would have a diameter of 7.0μ . A particle selected so that the total area or volume of all the particles above or below it were equal would have a diameter respectively of 21.0 and 36.4μ . This brings out the fact that a mean particle size has no significance unless the type of mean is specified.

2. **Structure.**—The macrostructure of refractories is of importance because a homogeneous material is seldom encountered. The size and shape of the pores, the shape of the grog particles, and the extent of the bonding are of interest. By a study of the structure, the manufacturing methods may be improved to produce a better product.

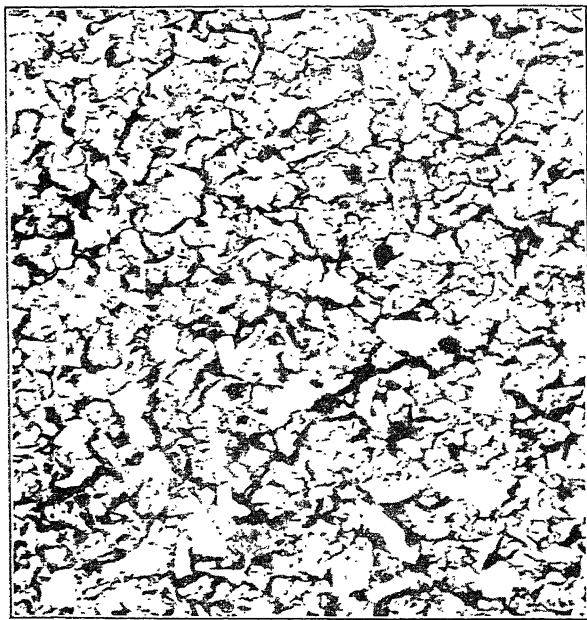


FIG. 328.—Structure of a kaolin refractory. The surface of this refractory was ground to a rough surface and then the pores were filled with sealing wax. The surface was then given a finer polish.

A cross section of a brick can be ground to a flat surface on a cast-iron wheel with coarse carborundum and water. The brick is then dried and heated enough to flow red sealing wax over the surface and into the pores. This surface can now be polished with a fine abrasive. The contrast between the light refractory and the dark sealing wax should bring out the structure very clearly. The structure of a kaolin brick prepared in this way is shown in Fig. 328.

3. **Permeability.** *Importance in Refractories.*—The flow of gases through refractory walls is important in many furnaces, especially where large pressure differences exist, as in recirculating types. Also the permeability of such parts as thermocouple tubes, muffles, and recuperators is of interest in efficient design.

Permeability is also of value as a check on the manufacture, as laminations, voids, and soft spots are shown up in the permeability test. In the case of heat insulators, this property is useful in indicating the extent of interconnecting pores.

Measurement of Permeability.—Absolute permeability is the property of the refractory and does not in any way depend on the fluid. It may be expressed as

$$\lambda = \eta \frac{Q}{A} \cdot \frac{l}{(P_1 - P_2)} \cdot \frac{1}{t}$$

where λ = the absolute permeability

η = the viscosity of the fluid, poises

Q = the volume of gas flowing at mean pressure $(P_1 + P_2)/2$, cc.

A = the area, sq. cm.

l = the length of path, cm.

P_1 = the exit pressure, dynes per sq. cm.

P_2 = the entrance pressure, dynes per sq. cm.

t = the time, sec.

The dimensions of this equation are L^2 = area. However, our usual measurements of permeability are with a particular fluid such as air at room temperature, so that the measured permeability k is expressed by

$$\frac{\text{Volume of gas} \times \text{length of path}}{\text{Area} \times \text{time} \times \text{pressure difference}}$$

which has the dimension

$$\frac{L^2}{ML^{-1}T^{-1}} = \frac{\text{area}}{\text{viscosity}}$$

k is usually expressed as cc. · cm. · sq. cm.⁻¹ · sec.⁻¹ · cm. of water⁻¹, or as cu. ft. · in. · sq. ft.⁻¹ · min.⁻¹ · in. of water pressure⁻¹.

✓ Permeability can be measured on small cylindrical or cubical specimens, but a more representative value is obtained on a whole brick with air passing through as it does in the wall. Permea-

bility tests of whole wall sections give data in regard to the joints and bricks together; but little work has been reported along these lines.

A precise and convenient apparatus for the measurement of permeability is shown in Fig. 329 as developed in the Ceramic Laboratory of the Massachusetts Institute of Technology. The

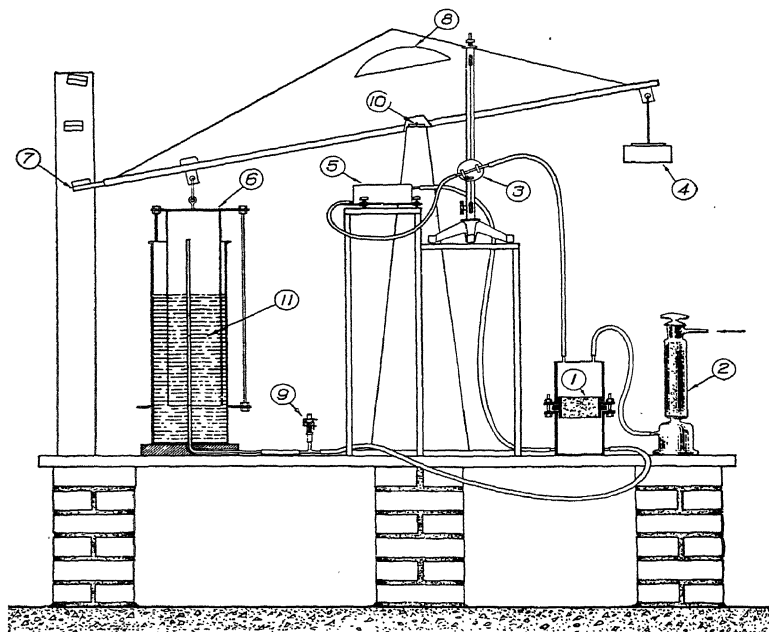


Fig. 329.—Permeability apparatus.

specimen 1 is cemented tightly into the holder with beeswax. Air is drawn through the drying tower 2 and the specimen by the suction of the gasometer 6 filled with oil 11 and counterweight 4 using a beam pivoted at 10. The latter is calibrated so that as it moves through a definite distance by the pointer 7 which can be timed with a stop watch to pull a known volume of air through the specimen. The balance weight 8 compensates for the buoyancy of the gasometer cylinder. The difference in pressure

between the two sides of the specimen is measured by the alcohol manometer 3 with its reservoir 5. The method of testing will be made clear by Table 92 for a typical run.

TABLE 92

Run No..

Weight on end of beam, g.	200	200	400	400	1,000	,000
Mercury below atmospheric pressure, mm...	0.85	0.85	1.70	1.70	4.24	4.24
Atmospheric pressure, mm. mercury.....	757.40	757.40	757.40	757.40	757.40	757.40
Pressure in gasometer, mm. mercury.....	756.55	756.55	755.70	755.70	753.16	753.16
Temperature, °C.....	29.0	29.1	28.4	28.3	28.0	28.1
V (from chart), volume of air at standard conditions passed through specimen, cc..	,604	1,604	1,595	1,595	1,592	,592
P ₀ , zero reading of manometer.....	1.16	1.16	1.06	1.05	1.06	1.06
P ₁ , final reading of manometer.....	1.41	1.40	1.52	1.51	1.94	1.94
P ₁ - P ₀ , pressure difference, cm. alcohol.....	0.25	0.24	0.46	0.46	0.88	0.88
Specific gravity of alcohol	0.801	0.801	0.801	0.801	0.801	0.801
P, pressure difference, cm. water.....	0.20	0.19	0.37	0.37	0.71	0.71
t, time, sec.....	119	120	68	69	34	34
K, permeability.....	5.6	5.7	5.3	5.3	5.5	5.5

Area of specimen = 78.5 sq. cm. Thickness = 6.5 cm.

Permeability values for several refractories are shown in Table 93.

4. Strength of Refractories.—The cold strength of fired refractories is not generally of importance in itself; however, it often serves as a guide to other characteristics such as vitrification, burning temperature, or purity of material. In the case of heat insulators, the strength is of value in determining the ability to withstand handling and shipping. Crushing strength is not the only factor that needs consideration, for resistance to abrasion is also important. In Table 94 are given values of crushing strength.

5. True Density.—The following method has been found satisfactory for the determination of true density: The material is powdered through at least 100 mesh, dried at 105°C. until thoroughly dry, and placed over CaCl₂ until at room tempera-

ture. About 1 g. is weighed into the previously calibrated and weighed pycnometer bottle. The bottle is filled about one-half full of freshly boiled distilled water; the bottle kept at 60°C.

TABLE 93.—PERMEABILITY OF FIREBRICKS (BURNED)

Type of clays	Manufacturing method	Permeability, cc per sec. per cm. cube per cm. head of water
Flint, semiflint, and plastic.....	Semidry press	0.0066
New Jersey plastic.....	Hand molded	0.0092
Semiflint.....	Soft mud	0.011
Flint and semiflint and plastic.....	Soft mud	0.012
Second grade semiflint and plastic.....	Soft mud	0.016
Plastic.....	Soft mud	0.017
Semiflint.....	Soft mud	0.033
Cheltenham plastic.....	Dry press	0.049
Flint and semiflint.....	Hand molded	0.069
Flint and plastic.....	Hand molded	0.11
Flint and plastic.....	Soft mud	0.13
Grog, flint, and plastic.....	Soft mud	0.14
Pennsylvania clay.....	Dry press	0.15
Second grade semiflint and plastic.....	Dry press	0.19
Sillimanite and clay.....	Hand molded	0.45
Silicon carbide, recrystallized.....	Dry press	0.80
Clay and carbon, insulating.....	Dry press	1.20
Insulating firebrick, 3.5 lb.....		2.6
Insulating firebrick, 3 lb.....		3.1
Insulating firebrick, 2 lb.....		5.5

TABLE 94.—CRUSHING STRENGTH OF REFRACTORIES

Material	Crushing Strength, lb. per sq. in.
Fireclay brick.....	2,000–12,000
Bauxite brick.....	6,000
Silica brick.....	3,000–5,000
Zirconia.....	7,000
Magnesite.....	5,000–8,000
Chrome.....	6,000
Insulating brick.....	50–500

for about $1\frac{1}{2}$ hr.; and the contents agitated to wet the particles thoroughly and remove entrapped air. The bottle is next placed under a vacuum to make certain that all air has escaped. The reduced pressure should not be strong enough to boil the

water violently, since loss is likely to occur. About 20 min. of treatment using an ordinary aspirator pump is sufficient.

The bottle is then filled to the mark with distilled water and placed in a constant-temperature bath for 1 hr., whereupon the bottle is carefully capped; the capillary and the outside of the bottle wiped clean; and the whole weighed.

The specific gravity is calculated from

$$\text{Specific gravity} = \frac{W - P}{(W_1 - P) - (W_2 - W)}$$

where P = the weight of pycnometer and stopper

W = the weight of pycnometer and stopper and sample

W_1 = the weight of pycnometer and stopper full of water

W_2 = the weight of pycnometer and stopper and sample and water

Tetrahychonaphthalene or tetrachlorethane, because of their low viscosity and high wetting properties, are useful in the case of nonplastics in place of water, as the boiling and deairing steps are eliminated. Values on the same sample should check to ± 0.005 .

6. Abrasion Resistance.—Refractories used in the hearths of furnaces or other places where objects are slid along them must have a good resistance to abrasion. Furthermore, refractories are often worn away by particles in a rapidly moving gas. Abrasion tests at room temperature, such as are regularly used for paving brick and tiles, mean little for refractories because the conditions are far different at high temperatures. In the first place, the refractory must have a strong, well-bonded structure, and secondly it must not become plastic at the working temperature. In general, it has been found that a brick that shows good resistance to load will also resist abrasion.

Abrasion has been measured at room temperature by the Bauschinger disk grinder, the sand blast of Bradshaw and Emery,⁽¹⁾ and the rattler test of the National Paving Brick Manufacturers' Association. None of these tests, however, is used at the working temperature of the refractory. Perhaps the most logical tests are those proposed by King.⁽²⁾ Here samples of the refractory are rubbed together inside a furnace, and the loss in weight determined for a certain time of test. To show the effect of temperature, a specimen was tested as follows:

Temperature of Test	Loss in Weight, %
20°C. (68°F.)	0.115
1050°C. (1922°F.)	0.255

This shows that the abrasion resistance decreases with the temperature. It was also concluded that a fine-grained structure and a high-burning temperature increase the abrasion resistance.

The abrasion resistance of an insulating firebrick is naturally less than for a heavy refractory, although hard coatings are helpful. Abrasion tests have been made on this material by circulating fine particles by means of a high-velocity air stream through a duct lined with a particular brick.

7. Electrical Resistivity.—In electric-furnace work, the electrical resistance of refractories is of considerable importance, and there are many other cases where a high-temperature electrical insulator is desirable.

The method of measuring the resistivity is theoretically simple but at high temperatures is beset by numerous practical troubles; however, at temperatures up to 1000°C. (1832°F.), the apparatus is comparatively simple. The methods used by the U.S. Bureau of Standards,⁽⁴³⁾ King,⁽⁴⁶⁾ Northrup,⁽³⁹⁾ and Brace⁽⁴¹⁾ are substantially the same. A comparatively high voltage is placed across the specimen, and the current flow measured with a sensitive ammeter or similar device. The greatest difficulty is to reduce the contact resistance, and a number of methods have been used to prevent this error. Henry⁽⁴⁴⁾ and a few others used alternating current of 1,000 cycles to prevent electrolytic effects.

In Table 95 are given some values of electrical resistivity obtained by different experimenters.

It will be noticed that the values given in the preceding table are rather discordant in some instances. This may be due in part to the variation in specimens and in part to errors in experimentation.

At low temperatures, refractories conduct very slightly. As the temperature is raised, the conductivity increases rapidly until the melting point is reached, where electrolytic conduction occurs. With a pure material, the conduction would be low up to the melting point; but with the average refractory, liquid phases are formed by the impurities at relatively low temperatures, so that we get an early falling off of the resistance. In

TABLE 95.—ELECTRICAL RESISTIVITY, OHMS PER CENTIMETER CUBED

Material	Firing temperature	Temperature of test				
		700°C. (1297°F.)	1000°C. (1832°F.)	1200°C. (2192°F.)	1400°C. (2557°F.)	1500°C. (2732°F.)
Chemical porcelain ¹	1400°C. (2550°F.)	84,000	20,000			
Bureau Standards porcelain #152 ²	1450°C. (2640°F.)	550,000	251,000			
Beryl ³	1355°C. (2470°F.)	51,000	high			
Spinel ³	1185°C. (2160°F.)	infinite	120,000			
Sillimanite ⁴	1185°C. (2160°F.)	infinite	95,000			
Kyanite ⁴	1185°C. (2160°F.)	infinite	570,000			
Andalusite ⁴	1185°C. (2160°F.)	infinite	130,000			
Periclase ⁴	1185°C. (2160°F.)	infinite	2,120			
Ohio flint clay ⁵	1300°C. (2375°F.)	15,800	3,910	1,050	721	582
Kaolin ⁵	1300°C. (2375°F.)	30,200	36,300	11,460	846	681
Sillimanite ⁵	1300°C. (2375°F.)	46,700	49,000	11,500	4,290	3,150
Silica ⁵	1300°C. (2375°F.)	77,500	49,000	15,700	8,050	5,660
Magnesia ⁵	1200°C. (2175°F.)	35,000	4,780,000	94,700	2,780	615
Diaspore ⁵	1300°C. (2375°F.)	2,990	886		
Bauxite brick ⁶	17,200	6,100	2,200	1,100
Carborundum brick ⁶ (recrystallized).....	4.1	2.5	1.7	1.6
Carborundum brick ⁶ (10 per cent clay bond).....	197,000	29,500	10,000	8,590
Chrome brick ⁶	171	63	85	41
Freday brick ⁶	10,800	4,160	1,420	890
Freday brick ⁶	480,000	180,000	80,000
Freday brick ⁶	2,300	690	280
Freday brick ⁶	50,000	15,000	3,000
Magnesite brick ⁶	708,000	193,000	22,400	2,500
Magnesite brick ⁶	100,000	40,000	3,000
Magnesite brick ⁶	12,000	400	
Kaolin brick ⁶	50,000	15,000	3,000
Silica brick ⁶	300,000	62,000	16,500	8,420
Silica brick ⁶	380,000	125,000	63,000
Silica brick ⁶	2,400	710
Zirconia brick ⁶	131,300	1,230	300	
Zirconia brick ⁶	1,250	968	
Zirconia brick ⁶	7,710		412

¹ KING. ² HENRY. ³ NORTHUP. ⁴ WILKES. ⁵ STANSFIELD, et al. ⁶ BARTON and REYNOLDS.
⁷ HARTMAN. ⁸ BARTON and REYNOLDS. ⁹ ARNOLD.

general, a pure, high-melting-point material will give the best high-temperature, electrical resistivity.

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PART IV

Use

CHAPTER XX

REFRACTORIES IN THE IRON AND STEEL INDUSTRY

1. Introduction. *Dependence of the Industry on Refractories.*—The iron and steel industry is so dependent on refractories for efficient production that all the larger steel companies are themselves conducting research on refractories or are cooperating with the refractory manufacturers to obtain the best product for each position in the furnace. Unquestionably, in many cases, refractories capable of withstanding higher temperatures would permit more efficient production of steel and, in many cases, a better quality of steel. For that reason, a great deal of effort is being expended on the study of high-temperature refractories, particularly for the open-hearth furnace.

Future Developments.—A problem that requires solution in the future is the production for the open-hearth furnace of a roof brick capable of operating at 100 or 200° higher than the silica roof and still giving a satisfactory life. The economy of insulation is now being thoroughly appreciated in the iron and steel industry, and to accompany insulation we must have a better quality lining brick to stand the greater mean temperature imposed. In the heat-treating field, the development of lightweight refractories has been advancing rapidly and will undoubtedly show still further progress in the next few years. The possibility of making sectional furnaces of portable panels that can be built around the completely fabricated structure for heat treating is being rapidly developed and will become of more importance as completely welded structures are more widely used.

The disintegration of refractories under reducing conditions must receive more attention, and bricks capable of withstanding

this deteriorating influence more successfully will undoubtedly be developed.

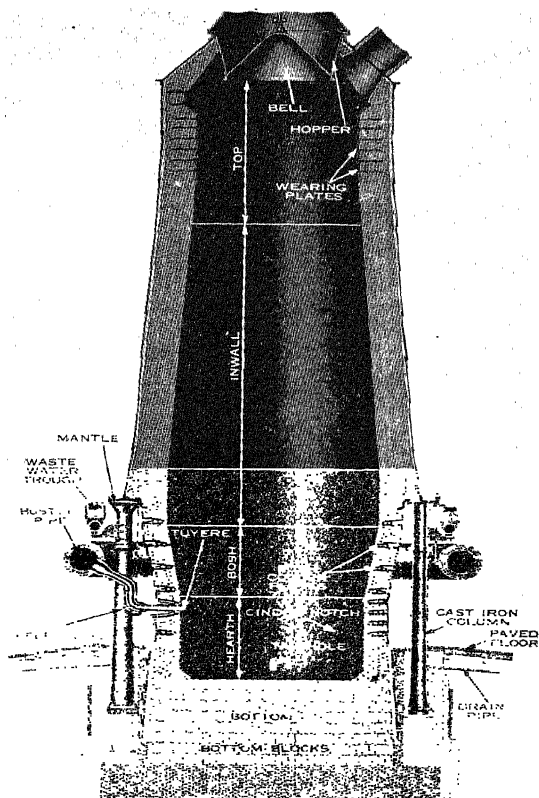


Fig. 330.—Typical modern blast furnace. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

2. Blast Furnace. *Principles of Operation.*—The blast furnace is the primary unit for reducing iron ore to iron. The charge, which is a mixture of iron ore, limestone and coke, is blasted with preheated air in the correct amount to generate heat and

form carbon monoxide, which reduces the ore to melted iron and slag. The composition of the iron depends a great deal on the type of ore used, but control of the final composition is possible in the blast furnace itself, except for manganese and phosphorus which cannot be greatly varied.

A Typical Furnace.—In Fig. 330 is shown the cross section of a modern blast furnace with the various parts labeled. It takes the form of a vertical shaft from 50 to 100 ft. high, with a hearth diameter of 18 to 27 ft. The refractories are completely surrounded by a steel shell. The charge is fed into the top of the furnace from a skip hoist through the double bell at the top and gradually passes down through the furnace as the reactions take place forming the iron and slag which collect in the crucible at the bottom. Periodically, the iron and slag are tapped off through separate notches.

It will be noted that the refractories in hotter parts of the furnace and sometimes in the lower portion of the inwall are heavily water-cooled by hollow metal castings extending well into the wall around the bosh and a water jacket extends down around the bottom, which is found necessary to give the long life needed for a satisfactory campaign, often lasting 2 to 5 years with a production of 1 to 2 million tons of iron. Water cooling has made feasible the use of a thinner wall than previously thought possible.

The gas from the top of the blast furnace, which is mainly carbon monoxide and nitrogen, is cleaned, and part is burned in the stoves which consist of a vertical, brick-lined steel cylinder partially filled with checker brick. These checkers are first heated up by burning the blast-furnace gas at the bottom, and then air is drawn through them in the opposite direction to be fed to the tuyères, producing an average preheat temperature of 1100 to 1500°F. As soon as the temperature of the stove reaches a certain minimum value, the flow is switched over to another stove that has previously been heated so that the cycle can be continued. Usually three stoves are used with one modern blast furnace. Modern design calls for taller stoves with insulation inside the shell.

The blast furnace and its stoves are large users of refractories, as approximately one million bricks would be employed in the construction of a modern unit.

Types of Refractories Used.—Practically all the refractories used in the blast furnace and stoves are fireclay brick. In the hearth and bosh are used high-flint clay bricks, which are generally vacuum extruded, dry pressed or air rammed, and high fired, to give a dense structure and low reheat shrinkage that will be resistant to slag and load under the severe conditions encountered in this part of the furnace. Accurate sizing of the blocks is desirable. The hearth bottoms are 9 to 12 ft. thick and are usually constructed of blocks larger than the standard 9-in. brick in order to reduce the number of joints. In spite of this construction, however, the bottom bricks are gradually eaten away or floated out during a long campaign and are replaced by iron, which solidifies and forms the salamander. A good description of the action on the hearth refractories is given by McLain.⁽⁹⁾

In the last few years, machined carbon blocks⁽¹⁰⁾ and rammed carbon plastics have been used for bosh and hearth linings in a number of German blast furnaces, but there seems to have been little work on such material in this country.

The bricks in the shaft of the furnace need not be so refractory as those in the lower part because the temperature decreases to approximately 400° at the exit. However, the bricks should be hard and resistant to the abrasion of the moving charge; and most important of all, they should be stable under the disintegrating effect of carbon monoxide, which was discussed more fully in Chap. XV. It is generally believed that if the iron in the bricks has been converted to iron silicate by high firing, little disintegration will occur. The shaft bricks also are subject to disintegration in the upper portions from metallic zinc, which is sometimes reduced from the ore, and, volatilizing, settles in the cooler portions of the lining, causing swelling and disintegration. Alkalies that are vaporized in the lower sections of the furnace also condense in the cooler parts and decrease the life of the lining.

Life of Refractories.—The nature of the blast furnace is such that little or no repairing can be done on the structure during a campaign, and therefore the life of the weakest part of the structure determines the total life. Usually the furnace must be shut down because of wearing away of the wall somewhere in the shaft, due to slag corrosion and abrasion. When the wall

becomes so thin that the temperature on the outside casing cannot be held down even by extra cooling, it is impossible to continue the furnace in operation. The modern furnace with thorough water cooling gives excellent life, and campaigns of

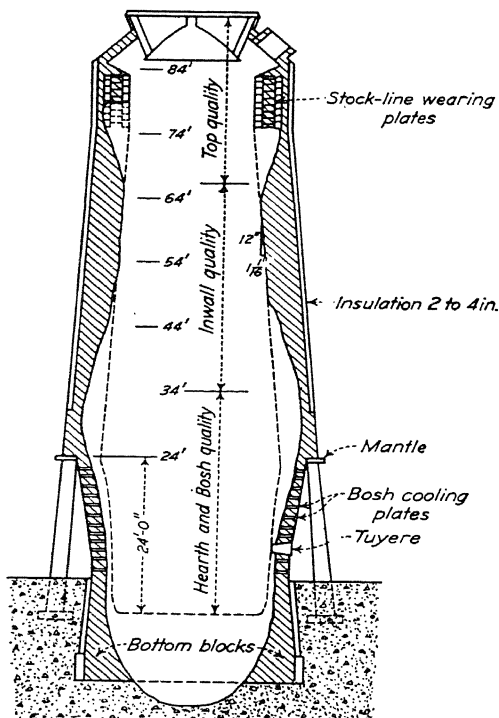


FIG. 331.—Burn-out lines of furnace. (Courtesy of W. R. McLain, *Bull. Am. Ceram. Soc.*)

3 to 5 years are commonly reported. In general, it would seem that the refractories available for the blast furnace are satisfactory for their purpose, but perhaps higher densities for the brick in the lower part of the furnace can still be achieved by more careful sizing of the raw materials, vacuum treatment, and higher pressures. Higher firing of the brick in the shaft

TABLE 96.—ANALYSIS OF SERVICE CONDITIONS IN THE BLAST FURNACE

Furnace Part	Material	Temperature, °F.	Slagging action	Abrasion	Load, lb. per sq. in.	Spalling	Life, years	Remarks
Top.....	Dense low-heat-duty fire-clay brick	400-600	None	Severe	Unimportant	Unimportant	3-5	
Upper inwall.....	Dense intermediate-duty fireclay brick	600-1000	Slight	Medium	Unimportant	Unimportant	3-5	
Lower inwall.....	Dense high-heat-duty fire-clay brick	1000-2000	Considerable	Slight	10-15	Unimportant	3-5	Disintegration by CO, Zn and alkalis
Bosh.....	Dense high-heat-duty fire-clay brick	2000-3300	Severe	Slight	20-30	Unimportant	3-5	Water-cooling plates to protect refractory from slagging
Hearth.....	Dense high-heat-duty fire-clay blocks. Also carbon blocks	2500-2900	Severe	None	May be high	Unimportant	3-5	Water-cooled jacket

will make them more stable in regard to disintegrating influences, but many problems still need study as far as these factors are concerned.

In Fig. 331 are shown⁽⁹⁾ the wear lines in a blast furnace at the end of a campaign. The first zone of wear is at the top under the stock-line wear plates and is due mainly to abrasion. The second zone is above the mantle and is caused by disintegrating influences of carbon monoxide, alkalies, and zinc, as well as slag erosion.

The checkers in the stoves show gradual deterioration due to slumping and shifting, but accurate pyrometer control to prevent overheating will minimize this condition. The use of super-duty fireclay brick in the upper portions of the checkers is generally recommended.

Table 96 gives an idea of the conditions encountered in the blast furnace.

3. Cupola. *Principle of Operation.*—The cupola is strictly a melting furnace using as a charge cast iron in the form of pigs, stove plate, and other scrap cast iron and in some cases scrap steel. The charge is alternately metal, coke, and some limestone as a flux. In a well-operated cupola, roughly 8 to 12 tons of iron can be melted to 1 ton of coke. The cupola itself is quite similar to the blast furnace in shape, consisting of a hollow shaft with a charge entering through a door near the top and the molten iron being tapped out periodically or constantly at the bottom. Air for combustion enters the lower part of the shaft through tuyères in the same way as for the blast furnace, but seldom is preheated air used in cupola melting. Unlike the blast furnace, the cupola is not used on continuous operation but is dumped each evening, repaired by patching, and started up the next day.

Typical Furnace.—In Fig. 332 is shown a cross section of a typical cupola for melting gray iron for foundry use. The shaft is completely lined with fireclay blocks molded to fit the curvature of the cupola. The door for charging is near the top of the shaft, and no attempt is made to collect the hot gases from the top. In the bottom of the shaft is a crucible for collecting molten iron, as clearly shown, together with the tap hole for draining off the melted iron. The bottom of the cupola can be dropped down at the end of a run for quicker cooling and easier repairs.

Types of Refractory Used.—The refractories used in the cupola are fireclay blocks made with a dense structure by hard pressing

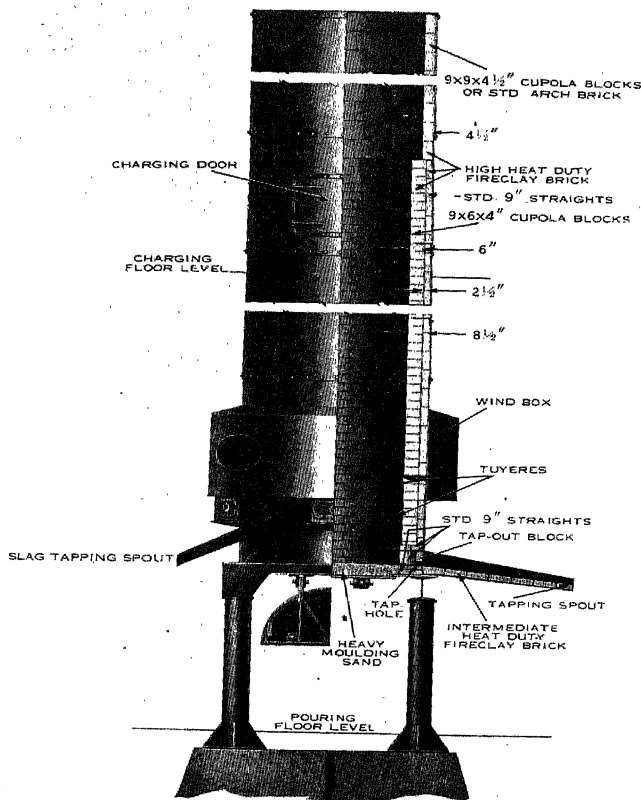


Fig. 332.—Section of typical cupola. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

or by deairing. Considerable improvement has been made in the cupola refractory in the last few years in the way of a more uniform and denser structure. Such a structure is more capable of withstanding the abrasion and slagging; but on the other hand,

because of the sudden temperature changes, the block must also have considerable resistance to spalling. Although the complete lining of the cupola lasts for a considerable length of time, perhaps for a year or more, it is necessary to make rather extensive repairs to the portion of the shaft around the tuyères every day by the addition of new blocks or simply by patching with a plastic material, which is usually made of crushed ganister and plastic fireclay.

Attempts have been made to line cupolas with a castable refractory consisting of grog, ganister, and high-alumina cement. Although this mixture has been used for patching in this country, the use of complete linings of this material has been confined in the past to European practice. Rammed linings are also used abroad because of their low cost. In Table 97 are given some of the conditions encountered by the refractory.

4. Open-hearth Furnace. *Principles of Operation.*—The open-hearth furnace is a reverberatory type with a flame playing over a relatively shallow layer of metal. The charge may be pig iron, either solid or in the molten state directly from the blast furnace; most generally pig iron and scrap; or scrap and carbon. The reactions occurring in this furnace are mainly an oxidation of the carbon, elimination of the phosphorus in the basic process, and a decrease in the silicon, manganese, and sulfur. In the acid process (siliceous slag), it is impossible to eliminate the phosphorus; accordingly, only low-phosphorus materials can be used, which in this country, limits the production of acid open-hearth steel to about 5 per cent of the total. For this reason, only the basic process will be considered here.

The output of the open-hearth furnace is mostly used for casting steel ingots, which are later rolled, hammered, or pressed into the desired shapes.

The fuel used in the open hearth is most commonly producer gas, but furnaces are fired by natural gas, fuel oil, tar, coke-oven gas, and even pulverized coal. The type of fuel governs the design of ports in the furnace and has a considerable influence on the life of the refractories. For example, producer gas gives a long flame that has a tendency to heat up the end walls and downtakes, whereas the coke oven gas has a hot flame that tends to heat the roof near the burner end of the furnace. All open-hearth furnaces are of the regenerative type, in which the

outgoing gases heat checker chambers. After a period of time, the flow is reversed and the incoming air and gas are preheated by passing through these hot chambers and then combined at the ports to form the combustion flame. Neither coke-oven nor natural gas can be preheated because of the tendency to crack.

Typical Furnace.—In Fig. 333 is shown a cross section of a typical stationary 100-ton basic furnace, which is an average size. Most of the furnaces are of the stationary type but a few tilt on a horizontal axis for pouring and to make up the back wall. The tilting makes the operation of the furnace somewhat simpler, but the initial cost is much greater, and there is some difficulty in making the air and gas connections tight. If anyone is interested in more detailed construction of the open-hearth furnace, he should refer to the excellent books by Buell.

The hearth of the furnace is built up on steel plates, as shown in Fig. 333, with a layer of insulating brick, magnesite or chrome bricks, or a rammed mixture and then a fritted magnesite bottom which is constantly being repaired during the campaign to maintain its normal thickness. The front and back walls of the furnace are usually made of silica brick with burned magnesite brick in the

TABLE 97.—ANALYSIS OF SERVICE CONDITIONS IN THE CUPOLA

Furnace part	Material	Temperature, °F.	Slagging action	Abrasion	Load	Spalling	Life	Remarks
Shaft lining, upper.....	High-heat-duty fireclay blocks, 9 × 6 × 4 in.	500–2000	None	Severe	Light	Important	1 year	Patching required every heat
Shaft lining, lower.....	High-heat-duty fireclay blocks 9 × 6 × 4 in.	2000–3000	Severe		Medium	Slight	1 year	
Bottom.....	Rammed sand and clay	2900	Severe		May be important	None	1 heat	
Tapping-spout lining...	Intermediate-heat-duty bricks	2000–2800	Slight	Cutting by metal	None	Severe	20–30 heats	

lower courses; but recently, chemically bonded brick of magnesite and metal-cased magnesite brick have been successfully used. A layer of chrome brick is usually introduced between the silica and magnesite brick.

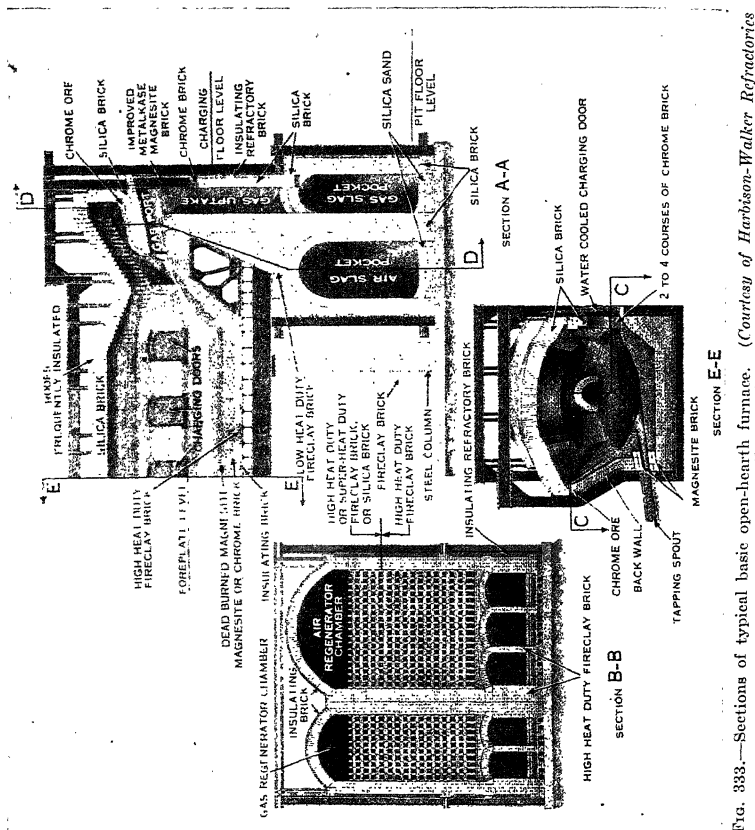


Fig. 333.—Sections of typical basic open-hearth furnace. (Courtesy of Harbison-Walker Refractories)

The end walls and bulkheads are built up of silica, magnesite, or chrome brick; but here again, the metal-case brick have proved quite satisfactory in many installations. The ports are usually

constructed of silica brick, but chrome and magnesite brick are used to withstand the slag and cutting action of the high-velocity dust-laden gases. Chromite ramming mixtures are sometimes used over the silica brick.

The doors of the furnace usually have water-cooled frames, which protect the brickwork from the mechanical abuse of the charging machine and give sufficient cooling to prevent deterioration of the front wall—a difficult portion of the furnace to repair.

The roof of the open-hearth furnace is one of the most important portions of the structure, because the life of the furnace as a whole is more or less determined by the life of the roof. Generally, the refractories used in the sprung arch of the roof are silica brick of $13\frac{1}{2}$ or 18 in. thickness. As the temperature required to maintain a low-carbon steel for pouring is 1585°C . (about 2880°F .), and the temperature at which the silica brick in contact with iron oxide begins to soften is 1650°C . (about 3000°F .),⁽⁴⁵⁾ it will be seen that only a small operating interval is available and that for this reason, the temperature control must be carefully maintained. In the modern plants, the roof temperature is read with optical pyrometers; and in some cases, temperature controllers operating on a radiation-pyrometer principle are permanently installed to cut off the fuel whenever the temperature exceeds the upper limit.

It might be thought that the silica brick, because of its tendency to spall, would be unsatisfactory in a regenerative furnace where a periodic change in temperature occurs at each reversal. However, if one would examine the expansion curve of a silica brick as shown in Fig. 298 of Chap. XVI, it will be noticed that above the red-heat range, the volume of the brick is substantially constant and changes in temperature in the higher zones will cause no appreciable volume change. In other words, the silica brick is unexcelled for these particular conditions and this constant volume at high temperatures explains why such good results are obtained with them.

Steel manufacturers have long desired a roof brick with a higher temperature range than silica, because it is obvious that, if the open hearth could run at 200 or 300°F . higher temperature, production from a given unit could be greatly increased and, at the same time, qualities of steel that now can be produced only in the electric furnace could be turned out more cheaply

In lining a ladle, the common practice is to use a thickness of $2\frac{1}{2}$ to 9 in., depending on the size of the ladle, and modern usage seems to tend toward the use of 1 or $1\frac{1}{2}$ in. of insulation between the refractory lining and the steel shell. The ladle bricks, usually in two layers, should be uniform in size so that

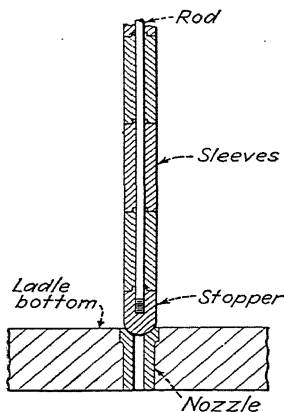


FIG. 334.—Nozzle and stopper assembly.

the thinnest possible dipped joints can be made. Care is necessary in drying out the ladle before use, which is usually done by building a fire of wood or coke in the bottom of the ladle or introducing gas burners. Practice varies in the time required for drying, some ladles being dried out in as short as 8 hr., and some in 48 hr. The life of the ladle lining depends to some extent on the type of steel, certain alloys being much more severe on the lining than carbon steel. Fluorspar, which is often used to increase the fluidity of the flux, has a severe action on the ladle lining and will often materially decrease its life. Smaller ladles for cast iron are often lined with a fire-clay plastic that must vitrify and give a hard surface.

Nozzles, Stoppers, and Sleeves.—The nozzle used in teeming steel from the ladle is a very important part of the ladle. A cross section of a typical nozzle and stopper assembly is shown in Fig. 334. A good stopper and nozzle should give a clean flow of steel without spattering at a substantially constant rate throughout the pouring operation, should be able to shut off the stream between ingot molds cleanly without dribbling, and it should be possible to open the nozzle on the first ingot without sticking.

In order to get a uniform rate of flow from the ladle, a material that will slowly erode and increase the diameter during the pouring operation must be used in the nozzle. It has been found that fireclay nozzles will have this property of giving a comparatively uniform flow rate from the beginning to the end of the pouring. On the other hand, a nozzle of magnesite is so resistant to erosion that it maintains substantially a constant

diameter and therefore the rate of flow decreases, as shown in Fig. 335.

In order to get a tight fit between the nozzle and stopper, it is usually desirable to have one of them slightly plastic, but not both, or sticking is certain to result. For this reason, either the nozzle or the stopper will generally be made of a more refractory clay than the other; or in many cases, the stopper would be made of graphite and clay, which are more rigid at the pouring temperature than the clay alone.

The steel rod attached to the stopper must pass down through the molten steel in the ladle and therefore must be protected with refractory sleeves. They are made of a fireclay, and it is particularly important that they resist cracking under the sudden heat shock. It is also important that the joints between the sleeves be carefully fitted so that the molten steel cannot force them apart.

In recent years, a great deal of interest has been shown in steel inclusions. It is beginning to be realized that many of these are due to particles of refractory from the ladle lining or from the nozzle and that the ability to produce really clean steel would seem to depend a great deal on finding a refractory that would be more stable than the fireclay refractory now used.

Tap Holes.—The tap hole in the open-hearth furnace must consist of a material strong enough to hold the pressure of the molten steel without breaking out and, at the same time, sufficiently soft to be knocked out with the tapping bar. It is general practice to make up a mixture of raw and burned dolomite for this purpose, although in some cases chrome-base cements have been used.

Hot Tops and Plugs.—The plugs are used at the bottom of certain ingot molds to receive the direct impact of the stream of molten steel from the ladle. They must, therefore, be resistant to spalling and at the same time sufficiently dense to prevent

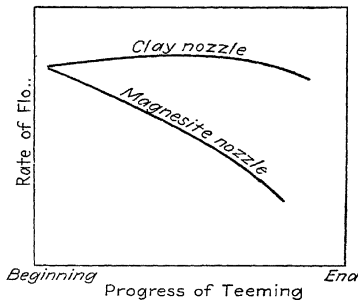


FIG. 335.—Flow of steel through nozzles.

erosion. They are usually made of a fireclay of comparatively low refractoriness and generally give little trouble.

The hot tops are placed on top of the ingot mold to prevent too rapid solidification of the top of the ingot and consequently a deep pipe. The hot tops must have a sufficiently close structure so that the steel will not penetrate them, and yet it is desirable to have them of light weight for low specific heat and low thermal conductivity with, at the same time, good spalling resistance. As they are usually only used once, the cost must be low. Generally, a comparatively low-burned fireclay mix is used, but some success has been had with lightweight refractories coated with a material to prevent penetration of the steel into the pores.

6. Air Furnace. *Principles of Operation.*—The production of malleable iron is generally carried out in the air furnace. The malleable iron is produced from mixtures of pig iron, steel, and malleable foundry scrap, which is refined in the furnace to produce the proper percentages of carbon, silicon, sulfur, manganese, and phosphorus. When the malleable iron is first cast, it has practically all the carbon in the form of carbide of iron, which gives a comparatively brittle structure. The cast objects are then subjected to a heat-treating process while packed in iron boxes, perhaps seven or eight deep, for a considerable length of time, after which the carbon is precipitated and gathers into regular nodules known as “temper carbon.” Sometimes the castings are simply annealed without packing. In the final condition, the metal is ductile and malleable and shows considerable elongation.

Typical Air Furnace.—Figure 336 shows a section of a typical air furnace, which consists of a shallow hearth made of silica sand and a firebrick wall and crown to cover it. An average-size hearth is 6 by 20 ft. with a capacity of 15 tons, but furnaces up to 50-ton capacity have been made. Unlike most reverberatory furnaces, the crown is not fixed but is composed of separate bungs in which a ring of bricks comprising a section of the arch is clamped in an iron framework. In this way, one or more bungs can be lifted from the furnace at any time with a crane and the furnace charged through the opening thus produced. The fuel used for heating this type of furnace may be coal, oil, or gas, but powdered fuel is, perhaps, most used. This

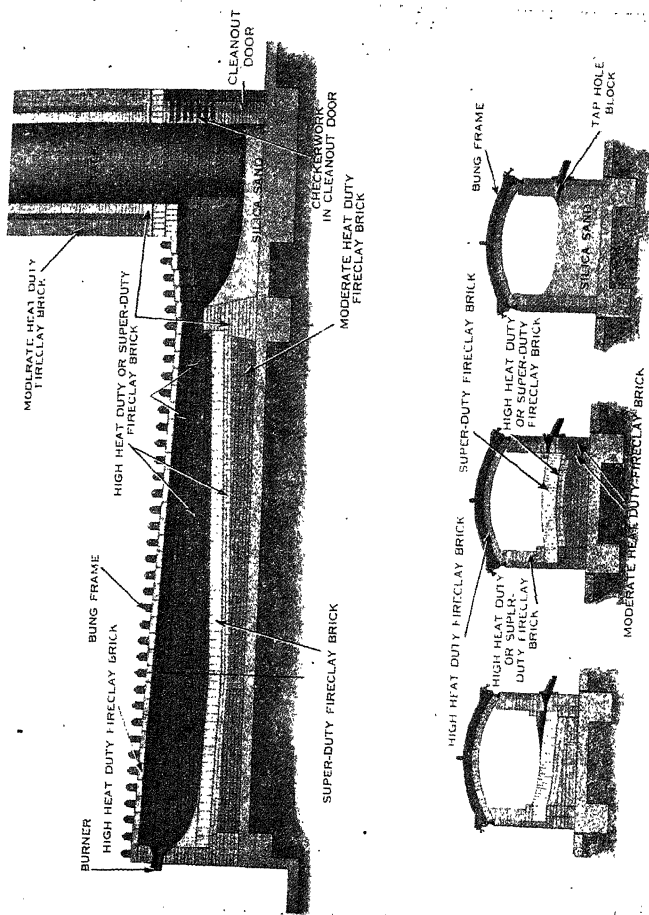


Fig. 336.—Pulverized coal-fired reverberatory furnace for malleable iron. (Courtesy of Harbison-Walker Refractories Company.)

TABLE 99.—CLASSIFICATION OF REFRACTORIES FOR MALLEABLE-IRON INDUSTRY
(Adapted from Industrial Survey of Conditions Surrounding Refractory Service in the Malleable-iron Industry, "Manual of A.S.T.M. Standards on Refractory Materials")

Part (see Fig. 336)	Material	Temperature	Spalling	Slagging	Load	Abrasion	Life	Remarks
Air furnace	Fireclay brick	Up to 3000°F. (1650°C.)	Very important where bungs removed for charging immediately after tapping	Minor importance	See note under "Remarks"	Important near back bridge wall	20-30 hours	The brick in the bungs are subjected to pressure that may be as high as 1000 lb. per sq. in. owing to setting up the clamps too tightly. This would be increased considerably as a result of thermal expansion when the bungs were heated up
Side walls	Fireclay brick	From 3000°F. (1650°C.) at front to 2400°F. (1315°C.) at back	Important above the slag line	Important from the hearth up to the slag line	10 lb. per sq. in. max.	Unimportant		
Bottom	Fireclay brick or silica sand	Varies from plant to plant and stage of melting operation. Approximately that of the metal	Minor importance	Important especially in "Dripping"	Minor importance	Important		

Part (see Fig. 336).	Material	Temperature	Spalling	Slagging	Load	Abrasion	Life	Remarks
Stack lining	Fireclay brick	2400°F. (1315°C.) max.	Unimportant	Unimportant	Depends upon construction. 50 lb. per sq. in. max. Usually an inner lining is built to a height of 15 to 20 ft. The load here is not in excess of 15 lb. per sq. in.	Unimportant		
Annealing oven	Waste heat boilers	2400 to 2600°F. (1315 to 1425°C.)	Moderate		Unimportant	Unimportant		
	Air preheaters	2400 to 2600°F. (1315 to 1425°C.)	Moderate	Unimportant	Unimportant	Unimportant		
	Combustion chamber	2100°F. (1150°C.) See note under "Remarks"	Moderate	Moderate	Unimportant	Unimportant		Some continuous ovens are oil-fired and higher temperatures prevail particularly in the bridge wall. Super-duty fireclay brick, high-alumina brick and silica brick are then used
Doors	Fireclay brick or insulating refractories	1600 to 1800°F. (870 to 980°C.)	Unimportant	Unimportant	Unimportant	Unimportant		
Walls	Fireclay brick or insulating refractories	1600 to 1800°F. (870 to 980°C.)	Unimportant	Unimportant	15 lb. per sq. in. max.	Unimportant		

produces rapid heating and comparatively high temperatures; consequently the crown of the furnace receives considerable abuse. A furnace is brought up to heat in $1\frac{1}{2}$ hr. and held 5 to 8 hr. The bungs have a comparatively short life of 20 to 30 heats, as a result of the rapid heating and cooling, but the side and end walls give generally good service. In Table 99 is given a summary of the service conditions in the air furnace.

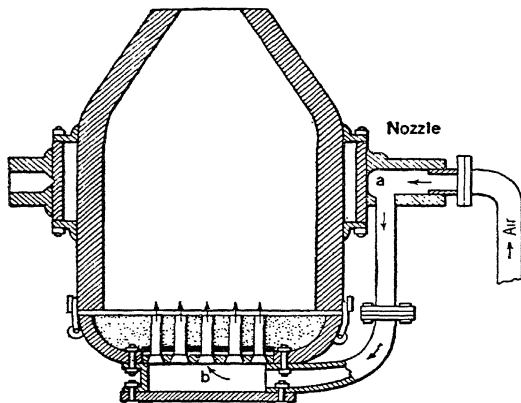


FIG. 337.—Bessemer converter. (From "Iron and Steel," by H. M. Boylston.)

7. Bessemer Converter. *Construction and Operation.*—The Bessemer converter is a pear-shaped, refractory-lined vessel on trunnions which permit it to be tilted from the horizontal to the vertical position. The bottom consists of a refractory containing a large number of holes through which air can be blown under considerable pressure. A typical converter is shown in Fig. 337.

In operation, the converter is charged with molten iron from the mixer or blast furnace while on its side. It would then be rocked into an upright position after the air blast had been applied, thus forcing air up through the molten metal and oxidizing the carbon and silicon to bring it down to the right composition.

Type of Refractory Used.—Most of the converters are acid lined with silica brick or natural furnace stone such as sandstone

or mica schist. The bottoms of the converter are usually made of fireclay and must be frequently replaced, as 10 to 30 is the average life. The walls of the converter, however,

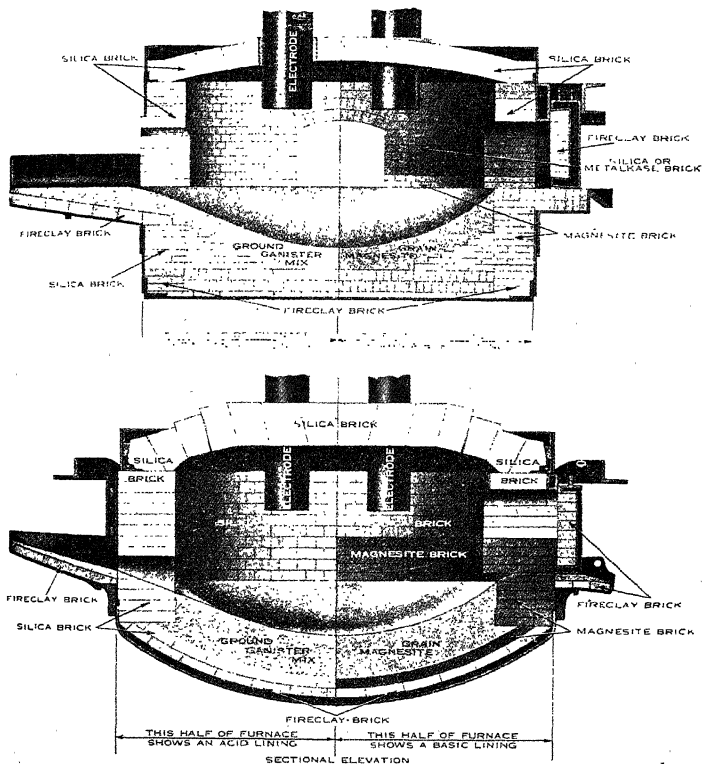


Fig. 338.—Typical electric steel-melting furnaces. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

may give a life of 200 or 300 heats before extensive replacements are necessary. ✓

8. Electric-arc Furnaces. Principle of Operation.—Furnaces of this type are used to melt iron and steel by the heat of an arc formed between the slag layer and the overhead electrodes,

usually three in number, which can be raised and lowered to accommodate the changes in metal height and loss in electrode length. There are many variations in types of furnace, but most of them consist of a cylindrical, refractory-lined shell with a domed roof and a charging door in the side. Nearly all of them are on trunnions so that they are poured by tilting.

The acid-type furnace is used mainly for steel castings and iron, whereas the basic furnace is most commonly used for production of steel ingots.

Construction.—In Fig. 338 is shown a cross section of two typical electric basic furnaces. The bottom is composed of about 10 in. of rammed, dead-burned magnesite or electrically sintered magnesite, bonded with organic material or silicate of soda. Such a bottom will probably be patched every heat but, under these conditions, will give good service.

The lower side walls are constructed of magnesite brick; and for this purpose, a low-iron magnesite is often preferred, because of its better resistance to spalling. The upper side walls are usually made of silica brick.

The roof, which is in the form of a dome, is generally made of silica brick, using specially made shapes to fit around the electrodes. Good success has been obtained, however, with roof bricks of other materials such as super-duty fireclay, kaolin, and mullite, all of which are more resistant to spalling during the week-end shutdowns than the silica. An average roof will have a life of 100 to 150 heats, although a longer life is sometimes obtained.

9. High-frequency Induction Melting Furnaces. *Principle of Operation.*—This type of furnace melts metal by inducing in the charge high currents by means of an external coil surrounding the crucible. This furnace differs from all others in that the heat is generated directly in the metal itself and the crucible is not subjected to any other heating. High-frequency induction furnaces are made in small units for experimental melts of a few pounds up to 5-ton steel-melting furnaces. This kind of melting has certain advantages, particularly for alloy steels, in that a thorough stirring of the melt takes place and the analysis of the resultant steel can be accurately controlled.

Refractories.—In Fig. 339 is shown a cross section of a large high-frequency induction furnace for melting alloy steels.

The high-frequency current is carried by the water-cooled coil, inside which is a formed mica sleeve or troweled on sillimanite mix for coil protection. On the inner side of this is rammed a thin layer of refractory to form the melting chamber. For the highest efficiency, this refractory must be thin, and yet it must not crack during the melting operation. The preferred method of putting in this refractory is to ram it by hand inside a core made in the form of a steel or asbestos cylinder. The core can be withdrawn or melted out while, at the same time, fritting the surface of the refractory together into a strong mass.

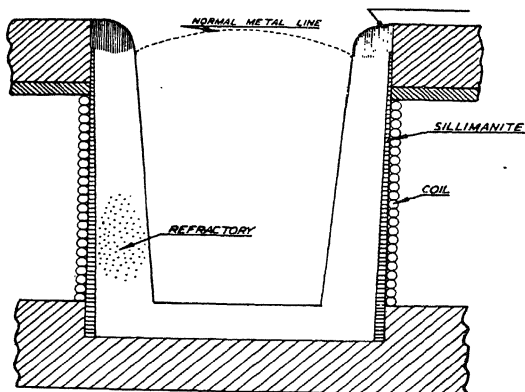
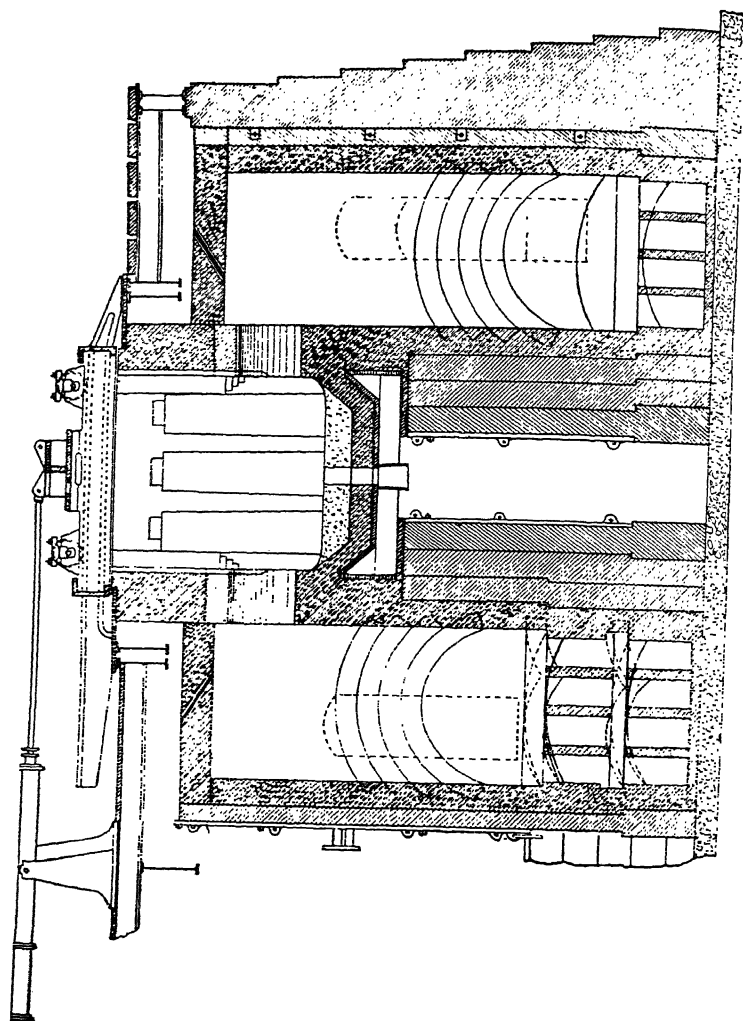


FIG. 339.—General arrangement of coreless induction furnace. (Courtesy of B. W. Magalis, Babcock & Wilcox Company.)

A satisfactory refractory may be a rammed ganister bonded with a little clay or silicate of soda for acid furnaces. Electrically sintered magnesite with an organic binder is used for basic furnaces, although linings are fritted in place with no bond by melting out an asbestos sleeve. With patching, 100 to 200 heats can be obtained with a single lining. Fused alumina and zircon have also been tried with good success in special cases.

For the smaller furnaces, prefired crucibles are generally used, magnesite being usually preferred.

10. Furnaces for Forming Operations. Soaking Pits.—The soaking pit as shown in Fig. 340 consists of a rectangular or



cylindrical furnace generally heated by tangential burners using either gas or oil as fuel. Regeneration is often employed. The removable cover, automatically operated, allows the heavy ingots to be placed or removed with an overhead crane.

The bottoms of these furnaces are made of rammed coke and molasses or rammed chrome plastic to withstand the action of mill scale, which forms in comparatively large quantities in furnaces of this type. The side walls are usually made of fireclay or silica brick, but unburned magnesite or chrome brick have been tried with success.

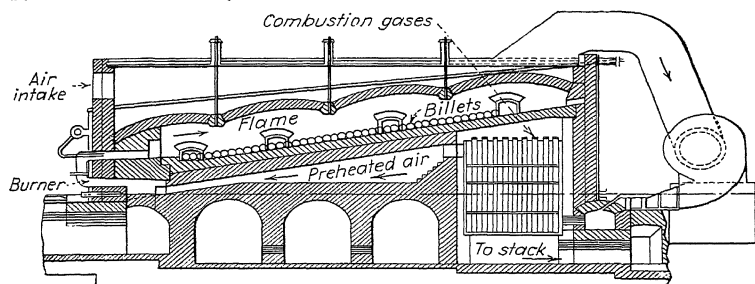


FIG. 341.—Continuous billet-heating furnace.

The cover is one of the most important parts of the furnace, as it must withstand considerable mechanical shock due to the frequent opening and closing; and at the same time, it should be as light as possible for the quick operation necessary for efficiency. For this reason, covers have recently been made almost entirely from insulating firebrick, because it not only reduces the weight of the refractory in the cover but also permits much lighter steelwork to be employed. These refractories must be carefully selected so that they will stand the spalling conditions of frequent opening and closing of the cover, have a light weight and a good insulation value.

Billet-heating Furnaces.—Billet-heating furnaces may be of the continuous type, a typical example of which is shown in Fig. 341. Here the billets pass through the furnace in a continuous layer on water-cooled rails and are heated mainly by convection of the hot combustion gases passing over and under them. This type of furnace is a true recuperative type, due to the counterflow action, so that the efficiency is comparatively high. The hotter

parts of the furnace are made of high-quality fireclay brick or kaolin brick, but the upper structure of the cooler portions is generally made from low-heat-duty brick with good insulation. The bottom of the furnace, which must resist the action of mill scale, is usually constructed of rammed chrome plastic at the hotter end.

Batch-type billet-heating furnaces are constructed in a large number of designs, but here the bottom is usually made of chrome

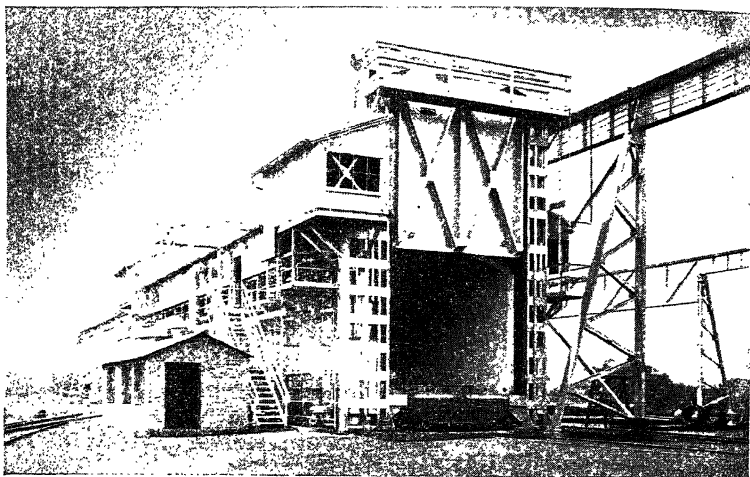


FIG. 342.—Large car bottom stress-relieving furnace. (Courtesy of Babcock and Wilcox Company.)

and the upper structure of insulating firebrick. The value of insulating firebrick is particularly evident in the doors, which are decreased in weight so that they can be operated more rapidly and with less discomfort to the workman.

Forging Furnaces.—Forging furnaces are made in many types. The refractory used is generally of fireclay, but the use of light-weight refractories is becoming quite prevalent in modern construction. The floor of the furnace may be of dense fireclay brick or rammed chrome plastic.

11. Heat-treating and Stress-relieving Furnaces.—Furnaces of this type are required to withstand only moderate temperatures. Heat-treating furnaces for high-speed steel might require

a maximum temperature of 2400°F., whereas stress-relieving furnaces would reach only 1400°F. For this reason, it has been found that the insulating firebrick can be used very successfully in many constructions. It has the advantage of giving a material saving in fuel, lower cost of burner equipment, and, in many cases, increased life.

In Fig. 342 is shown an illustration of a large car bottom stress-relieving furnace fired by natural gas which will take drums to 100 tons in weight. It is lined with insulating firebrick, thus giving a very uniform distribution of temperature as well as excellent fuel economy.

12. Bright Annealing Furnaces.—Furnaces of this type operate with a controlled atmosphere, usually with hydrogen. The temperatures are low; and for this reason, the insulating firebrick has seen extensive use both in the continuous and in the intermittent types. Because of the strong reducing action of the hydrogen, it is necessary to employ a refractory that will be stable under these operating conditions. For that reason, bricks low in iron oxide content are desirable.

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CHAPTER XXI

REFRACTORIES IN THE NONFERROUS-METAL INDUSTRY

1. Copper Production. *Outline of the Process.*—The common copper ores contain between 1 and 2 per cent copper and must be concentrated by ore-dressing methods, which bring the percentage of copper up to between 20 and 30 per cent. If this concentrated ore contains free sulfur or a too high quantity of iron sulfide, it must be roasted to drive off a portion of the sulphur as SO_2 . This roasting takes place at a low temperature in a multiple-hearth furnace (Fig. 343); and although no serious refractory problems are encountered here, the hearths of fireclay brick must be abrasion resistant. The roasted ore is then smelted, which is carried out at the present time in a reverberatory type of furnace, as the blast furnace is seldom used. In this operation, the copper sulfide is separated from the gangue and some of the iron as a matte, which is a mixture of copper and iron sulfide. This matte is then treated in a converter where air is blown through the melted sulfides, thus oxidizing the sulfur and the iron, the latter being taken up in the slag and the former passing out of the furnace as SO_2 . The crude copper, called "blister copper," is then treated in an anode furnace where it is further oxidized, and the base metal oxides formed are taken up in the slag and removed. The copper is then reduced by covering with coke and introducing green poles which give off CO and water vapor, thus reducing all but a very small amount of the copper oxide to metallic copper. The copper from this process is cast in anodes and treated in a cell to form electrolytic copper cathodes; at the same time, the gold and silver can be recovered in the slimes. The electrolytic copper cathodes are then melted in a refining furnace and cast into commercial shapes.

Reverberatory Smelters.—This type of furnace, as shown in Fig. 344, very much like a long open-hearth furnace, is fired at

one end, usually with gas, oil, or powdered coal. The charge, which in the earlier furnaces was fed through openings in the center of the roof, is now fed through openings in the roof near the skewbacks. As the charge melts, it flows down to the cooler

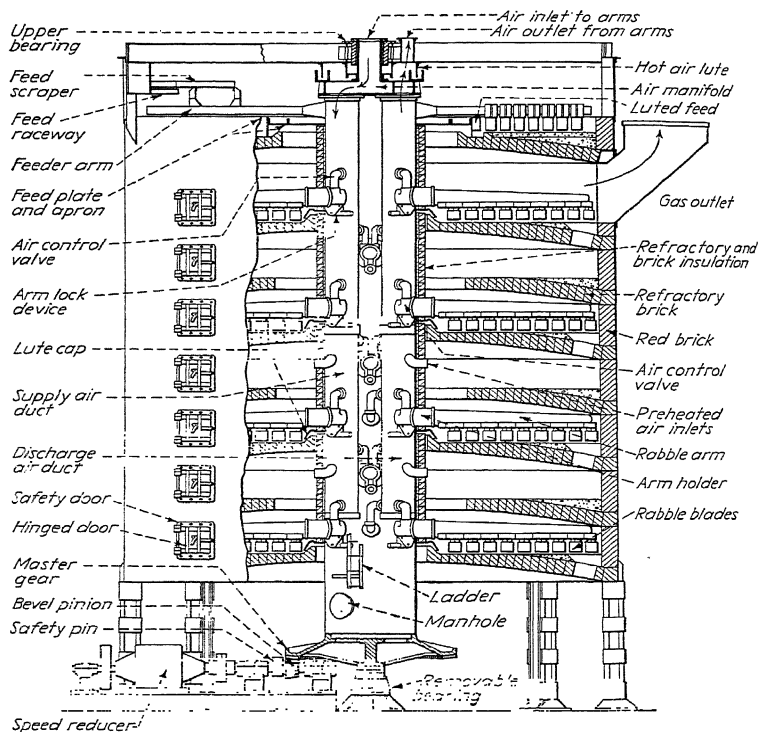


FIG. 343.—Wedge roaster. (Courtesy of Bethlehem Foundry and Machine Company, G. Thorpe.)

end of the furnace where the matte and slag can be tapped off separately. The size of these furnaces is usually 20 to 25 ft. in width and 120 ft. in length, capable of handling 500 to 1,000 tons of charge per day, although a few furnaces even larger than this have been constructed.

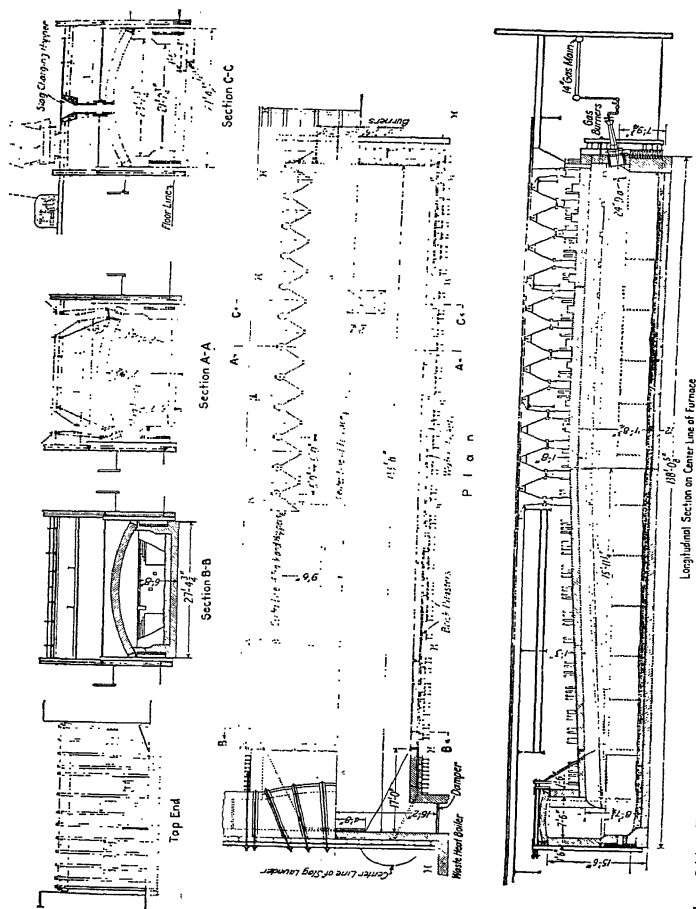


Fig. 344.—Reverberatory copper-mating furnace. (Courtesy of American Institute of Mining and Metallurgical Engineers, Paper by Frederick Laist.)

The bottom of the furnace is made of silica rammed in and fritted in place much in the same way as the acid bottom is put in an open hearth. The bottom must be sufficiently dense to prevent the penetration of the liquid matte and requires frequent repairs.

The side walls of the furnace are generally silica brick, although magnesite brick have been used in the lower side walls. Water cooling at the burner end has been used in some furnaces; but at present, it is not common. Silica brick are also used in the end walls, but high-alumina brick have also been successful in some cases.

The roof of the reverberatory furnace is exposed to a great deal of dust, which fuses and produces a severe slag attack. Silica brick are generally used in the roof in spite of the fluxing effect. Within the last few years, magnesite brick either of the hard-fired, low-iron type or chemically bonded brick have been used quite extensively in the portion of the arch near the skew-backs, especially around the charging holes. Suspended roofs of chemically bonded magnesite have been tried with very good success in Canada. The life of the silica roof runs about 100 days; but with the use of magnesite, a somewhat longer life has been reported. Insulation of these furnaces is beginning to be recognized as good practice, and probably all furnaces of this type will be insulated to some extent in the near future.

Copper Converters.—Two types of converter are generally used at present known as the "Great Falls" (Fig. 345) and the "Peirce-Smith" (Fig. 346). In the Great Falls type, the horizontal section is circular; whereas in the Peirce-Smith type, it is rectangular. The converters are mounted on trunnions for pouring the slag and metal, and the capacity runs from 100 to 300 tons per day. Converters are almost always lined with magnesite brick backed up with some magnesite grain between the lining and shell. Some unburned magnesite brick have been tried in converters, apparently with considerable success. The life of these linings is quite long, averaging 5 to 10 years, as a layer of magnesite is built up on the inner surface and protects the lining. Around the tuyères, however, the cutting action may be quite severe, and repairs have to be made in this zone after about six months or less.

Copper Anode Refining Furnace.—Most of these furnaces are of the reverberatory type, perhaps 35 ft. long and 15 ft. wide, with a capacity of 250 to 400 tons of copper. The fuel is oil, pulverized

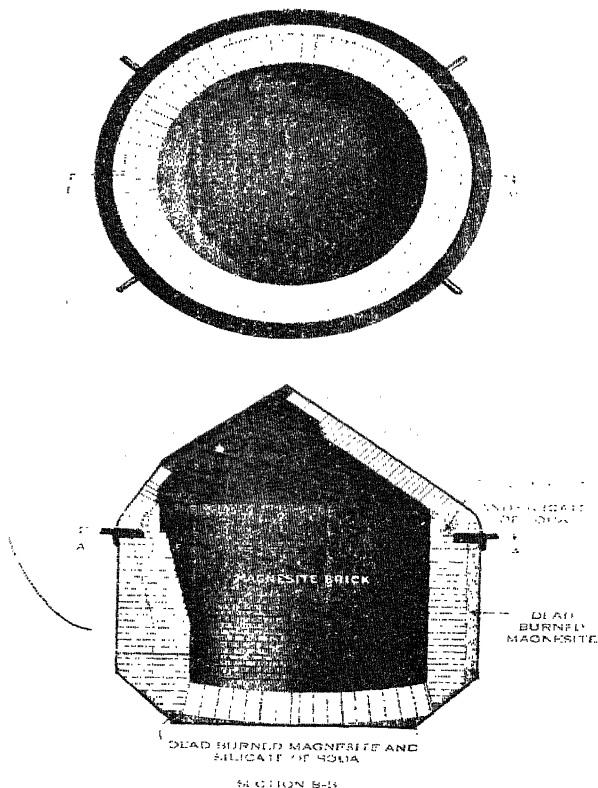


FIG. 345.—Copper converter, Great Falls type. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

coal, or gas, firing being from one end. After melting, air is blown into the bath to saturate with Cu_2O , while a small amount of siliceous flux is sometimes added to slag the base metals. The slag is then skimmed off; the charge covered with coke and

poled to reduce the Cu_2O . The refining cycle takes somewhere around 24 hr. The bottoms of these furnaces are quite similar to the bottoms of the smelting furnaces, *i.e.*, ganister rammed

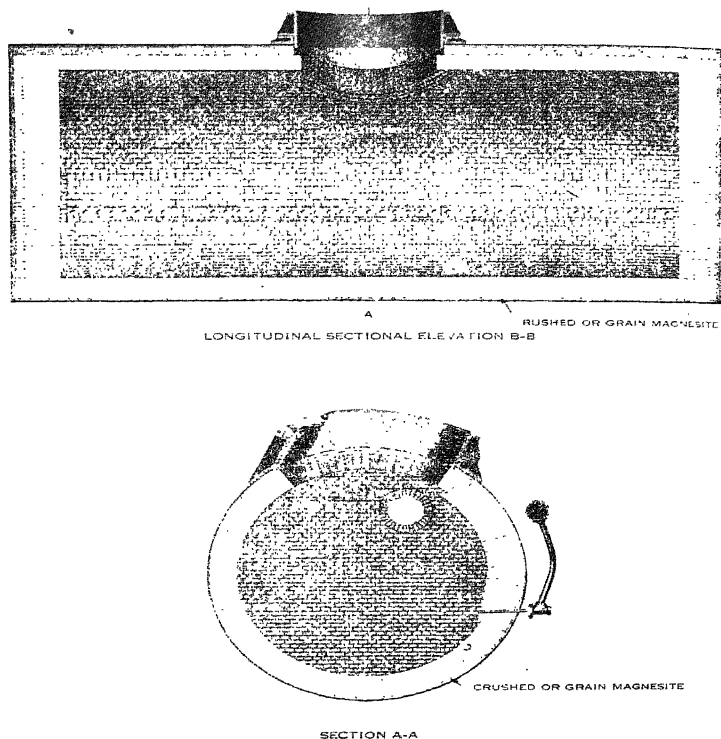


FIG. 346.—Copper converter, Peirce-Smith type. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

on top of clay brick. In the melting operation, at the surface of the ganister is formed copper silicate which acts as a cementing material to give a strong, firm body. Often bottoms are kept cool by air circulating through pipes running under the bottom. Although requiring occasional patching, bottoms may last from

3 to 5 years. In the side walls, magnesite brick are used to slightly above the slag line, beyond which silica brick are generally used. Above the slag line, chemically bonded and metal-cased magnesite brick have been successfully tried, giving a life of 200 heats.

The roof of the refining furnace is generally of silica brick, but it is actively attacked by the copper oxide slag thrown against it during the poling operation. Thus the roof has a life of only 100 to 125 heats. Magnesite and forsterite bricks have been tried in the roofs to some extent, with somewhat increased life.

Wire-bar Furnaces.—The operations producing wire bars and other commercial shapes from copper cathodes are practically the same as those for producing anodes. The furnaces are very similar to the anode furnaces previously discussed, except the bottom is made of silica brick instead of silica sand. Side walls are made of magnesite to slightly above the slag line, and either silica or magnesite brick are used

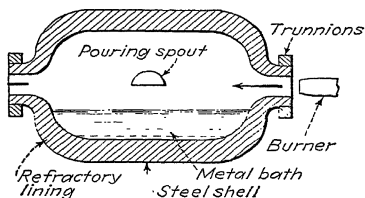


Fig. 347.—Open-flame brass-melting furnace.

up to the arch. In the upper parts of the side wall, both unburned and metal-case brick have been successfully tried. The roofs are usually made of silica, although magnesite brick have been used with a somewhat greater life.

2. Melting Copper Alloys. *Types of Furnace.*—The melting of brass and other copper alloys is carried out in gas- or oil-fired furnaces with a shallow hearth and an open flame; but for smaller lots or high-zinc alloys, plumbago crucibles are used. The indirect-arc furnace in a rotating cylindrical shell is much used, but recently, however, the induction-type melting furnace of the Ajax-Wyatt type is favored.

Open-flame Melting Furnaces.—In Fig. 347 is shown a tilting furnace of this type in which the oil burner is introduced through one end and the charge is put through a door in the side of the shell. The shell itself can be rotated on trunnions for pouring.

The linings of these furnaces are usually made from dense fireclay brick. For the hearth is used a rammed-in plastic

TABLE 100.—CLASSIFICATION OF REFRACTORIES FOR THE COPPER INDUSTRY
(Adapted from Industrial Survey of the Conditions Surrounding Refractory Service in the Copper Industry, "Manual of A.S.T.M. Standards on Refractory Materials")

Furnace part	Material	Temperature	Load	Spalling	Shaping action	Abrasion	Life	Remarks
Roasting Process								
Roasting furnace	Lining	High-heat-duty fireclay brick; insulating brick between lining and shell	1500°F. (815°C.), max.	Moderate	Slight	None		Important
	Hearths	High-heat-duty fireclay brick	1500°F. (815°C.), max.	Moderate arch stresses	Slight	None		Important
Smelting Process								
Smelting furnace, reverberatory	Side walls	Silica brick, magnesite brick	Approximately 2900°F. (1540°C.)	15 lb. per sq. in., max.	Slight	Severe		Moderate
	Bottom	Silica sand, silica brick, magnesite brick, chrome brick, silica sand largely used	2500 to 2800°F. (1370 to 1540°C.)	Unimportant	Unimportant	Severe		Moderate
	Roof	Silica brick, magnesite brick, suspended unburned magnesite brick, forsterite brick (in certain portions)	2800°F. (1540°C.), max.	Arch stresses in spring construction	Usually slight, although may be severe cause for premature failure	Important		Moderate
	Firewall	Fireclay brick, silica brick, magnesite brick	2850°F. (1565°C.)	10 lb. per sq. in., max.	Moderate	Important		Moderate
	Front wall	Silica brick, magnesite brick, fireclay brick, high-alumina brick	2400°F. (1315°C.), max.	10 to 15 lb. sq. in.	Slight	Severe		Moderate
	Waste heat boilers	Fireclay brick, silica brick	2300°F. (1200°C.), max.	15 to 20 lb. per sq. in.	Slight	Important		Moderate
							Conditions for direct coal fired. Where gas, oil, or powdered coal is used, combustion takes place in furnace proper	
							Waste heat boilers commonly used	

Furnace part		Material	Temperature	Load	Spalling	Slagging action	Abrasion	Life	Remarks
(Converting Process)									
Converter	Lining	Magnesite brick	2400°F. (1315°C.)	Unimportant	Temperature drops to 1200°F. during charging. Spalling unimportant for bottom half of lining; moderate for upper half	Moderate on basic lining	Erosion severe	5-10 years	
(Refining Process)									
Refining furnace	Furnace roof	Silica brick	2800°F. (1540°C.), max. 2300°F. (1260°C.), max.	High High	Moderate to severe Slight	Severe Severe on silica brick at junction of bottom and side wall Severe	Slight Severe High at charging doors	100-125 heats 3-5 years	
	Furnace bottom	Front walls and from bottom to just above metal line in back wall, magnesite brick Back walls { magnesite brick above net- silica brick at line } High-heat-duty fireclay brick Magnesite brick, high-alumina brick, silica brick, high-heat-duty fireclay brick High-heat-duty fireclay brick	2700 to 2800°F. (1480 to 1540°C.) 2800°F. (1540°C.), max. 2900°F. (1540°C.), max.	Moderate Moderate Moderate Moderate Moderate	Severe on magnesite brick Moderate to severe Moderate Moderate	Severe on silica or fireclay brick Varies with fuel Severe at intake Moderate	Slight Varies with fuel Moderate		
Holding furnace	Waste heat boilers	Usually magnesite brick	2700 to 2800°F. (1480 to 1540°C.)	Moderate	Moderate	Moderate to severe	Slight		
	Bottom and side walls	Silica brick, magnesite brick, forsterite brick	Approximately 2800 to 2400°F. (1260 to 1315°C.)	Roof high; remainder moderate	Moderate to severe	Moderate to severe	Slight		

mixtures, a Missouri fireclay generally being preferred in this country because of its good hot strength. Although the retorts

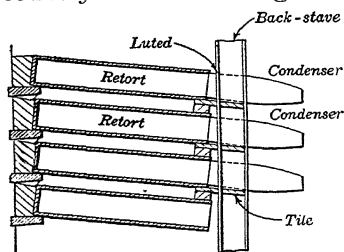


FIG. 350.—Details of zinc retorts and condensers. (From J. L. Bray, "The Principles of Metallurgy.")

used to be handmade, they are made, at present, entirely by machine, such as a hydraulic press. A good density of structure is necessary to prevent loss of zinc vapor through the walls and also to prevent too much zinc from being lost in the pores of the retort when it is rejected at the end of the run. Some plants find that retorts containing 75 to 85

per cent silicon carbide give enough greater life to pay for this more expensive material.

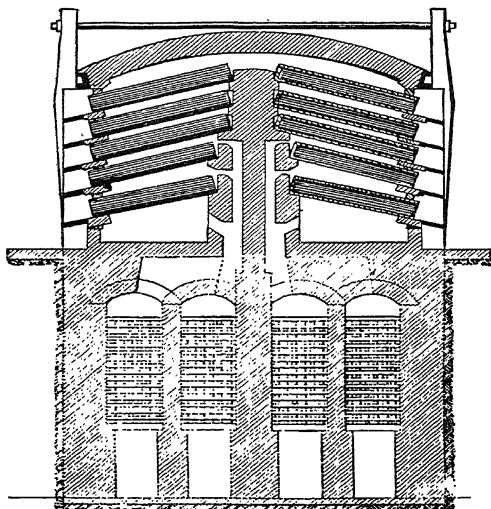


FIG. 351.—A cross section of a Belgian zinc distillation furnace. (From "An Outline of Metallurgical Practice," by C. R. Hayward, courtesy of D. Van Nostrand Company, Inc.)

These retorts with their condensers are set up in banks of 200 or 300 in a long gas-fired furnace, as shown in Fig. 351. usually of the Belgian type. A center wall running down the

middle of the furnace holds the back end of the retorts, whereas the front end is luted into the wall of the furnace. The firing is usually regenerative, and temperatures of 1250 to 1350°C. (about 2280 to 2460°F.) are reached inside the retorts, whereas outside temperatures as high as 1450°C. (about 2640°F.) are sometimes employed. This necessitates a rigid retort to carry the load at these temperatures, and it also means that the center wall of the furnace must be of a high-quality refractory. The side walls of the furnace are usually made of fireclay brick, whereas silica brick would be used for the center wall and roof. Hard-fired, high-alumina brick have been tried in the center walls and should give good results. The life of the retort runs from 30 to 40 days, but the furnace itself, being quite free from slagging action, gives a life of several years without repairs. Table 101 gives the service conditions for this type of furnace.

The Continuous Zinc Distilled Furnaces.—The continuous furnaces, as developed by the New Jersey Zinc Company, use a vertical retort constructed of silicon carbide with a section of about 1 by 5 ft. and a height of 20 to 25 ft. The briquetted charge of coal and zinc ore is continuously fed in the top, and the distilled zinc is collected in condensers around the top of the shaft while residues are discharged at the bottom. A single retort has a capacity of about 6 tons of zinc per day, and the life of the continuous retorts is estimated at 3 years. The furnaces in which these retorts are placed are fired with gas.

The Electrothermic Zinc Furnace.—This type of furnace has been described by McBride.⁽²⁵⁾ It is a vertical shaft heated by electrical resistance of the charge itself. The refractories composing the shaft must have a low porosity to prevent zinc penetration, high softening point, and high electrical resistance.

4. Lead. *Outline of the Process.*—Lead ores are usually sulfides, of which the mineral galena is most common. The ore is concentrated by selective flotation, and the lead concentrate is sintered to a firm mass, usually in the Dwight Lloyd type of continuous machine which does not employ any refractory. In this process, most of the sulfur is driven off as SO_2 and the lead is converted to an oxide. The process also produces the ore in a lump form, which is more suitable for the smelting operation. The smelting generally takes place in a water-jacketed blast furnace in order to slag off the impurities contained in the ore and

TABLE 101.—ANALYSIS OF REFRACTORY SERVICE IN THE ZINC INDUSTRY

Furnace part	Material	Temperature, °F.	Load	Spalling	Slugging	Abrasion	Life	Remarks
Retorts	Flint fireclay.	2280-2460	Important	Slight	Some	Slight	30-40 days	Silicon carbide re- torts have been tried 50 per cent alumina brick have been tried here
Condensers	Dense structure Flint fireclay.	Low	Low	Slight	None	None		
Smelting furnace side walls	Dense structure High-heat duty-fire- clay brick	2500-2640	Unimportant	Unimportant	None	None	2-3 years	
Smelting furnace center wall	Silica or super-duty fireclay brick	2500-2640	Important	Unimportant	None	None	2-3 years	
Smelting furnace roof	Silica	2500-2640	Arch stresses	Unimportant	None	None	2-3 years	

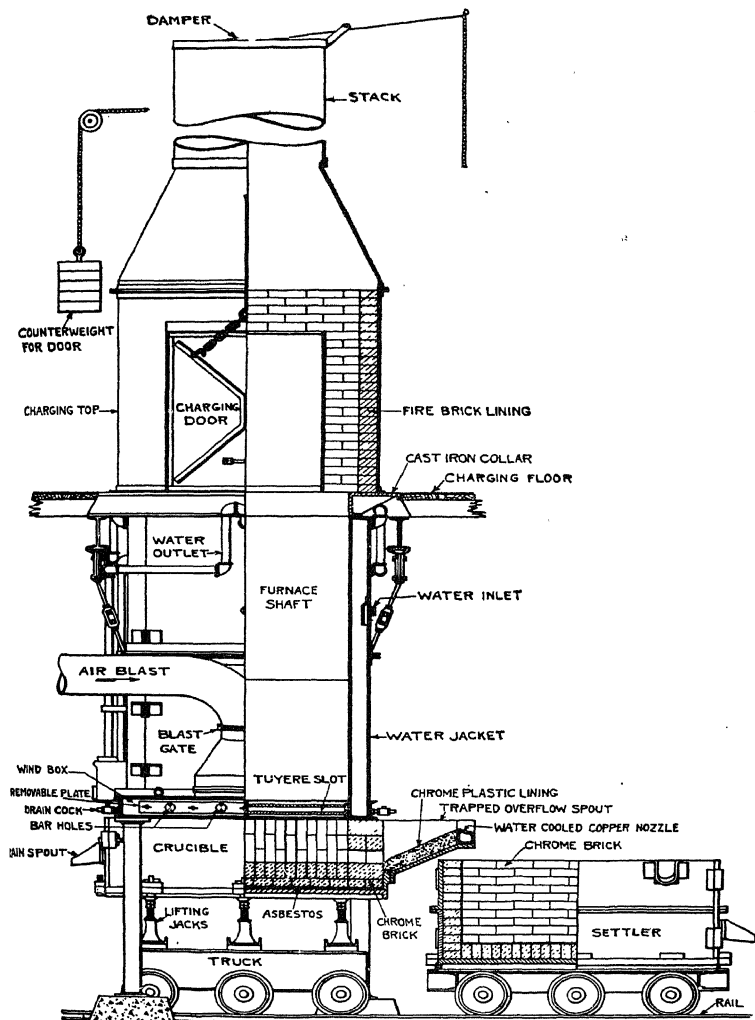


FIG. 352.—Sectional view of lead-smelting furnace, matting type with outside settling. (Courtesy of Mr. C. H. Mace, The Mace Company, Denver, Colorado.)

to reduce the lead oxide to molten lead. The larger part of the molten lead is removed from the furnace through a "siphon tap" which passes through the crucible wall to the bottom of the crucible. The slag with some occluded lead is tapped from the furnace and allowed to separate in a settler from which the slag overflows to a slag car. The lead is tapped out periodically.

The Lead Blast Furnace.—The lead blast furnace, as shown in Fig. 352, indicates that very little is used in the way of refractories because of the almost complete water jacket. However, there are refractories, usually high-duty fireclay brick of good density, in the upper part above the water jacket. Abrasion is the most important factor here, as the temperature is comparatively low. Refractories are also used in a crucible below the tuyères; but here again the temperature is not very high, and therefore the refractory requirements are chiefly low porosity and hardness and resistance to the action of molten lead. Dense firebrick are used in the crucible; but it is important that the joints between them be very thin, and often a chrome-base mortar is used for a jointing material. In some cases, plastic refractories of fireclay grog, ash, and coke are rammed into the crucible. Chrome plastics are also used to some extent, especially for the overflow spout.

Lead-refining Furnaces.—Molten lead that comes directly from the blast furnace or from the desilvering kettles is treated in a reverberatory type of refining furnace somewhat as shown in Fig. 353. Air is blown into the bath to oxidize iron, arsenic, antimony, and tin to dross, and the latter is skimmed off and retreated. High refractoriness is not required, as the maximum temperature is around 1100°C. (about 2000°F.). Temperature changes are not particularly great; consequently, spalling is not a problem. Slag action is the most serious trouble, as the action of lead oxide is very severe in contact with most types of refractories. Magnesite brick are now generally used in the side walls to somewhat above the slag line, but high-alumina brick have also been tried. The upper parts of the furnace may consist of a medium-duty firebrick with moderate resistance to spalling. The life of a brick in the upper wall depends a great deal on the type of operation and the amount of antimony in the lead.

5. **Tin.**—There are, at the present time, very few tin smelters in the United States; but in other countries, this is a

comparatively important operation. Many types of smelting are used, depending on the kind of ore. The metallurgist is fortunate in having, as his raw material, tin oxide, which can be readily reduced to the metal without great difficulty. The older types of furnace constructed are small blast furnaces much like

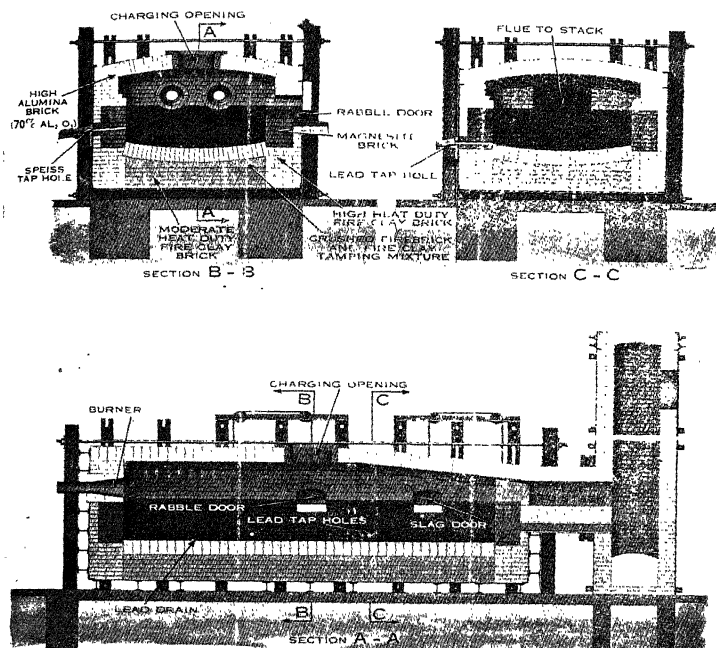


Fig. 353.—Typical lead-drossing furnace. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

the ones used for copper and lead. More recently, however, reverberatory furnaces have been used similar to those for copper ores, although on a much smaller scale. As the temperatures are comparatively low, and the tin oxide is not an extremely active flux, dense fireclay brick have been found adequate as refractories. ✓

✓ **6. Aluminum.**—Aluminum is produced by the electrolysis of fused salts, a process that calls for no particular amount of refrac-

TABLE 102.—CLASSIFICATION OF REFRACTORIES FOR THE LEAD INDUSTRY
(Adapted from Industrial Survey of Conditions Surrounding Refractory Service in the Lead Industry, "Manual of A.S.T.M. Standards on Refractory Materials")

Class	Furnace part	Material	Temperature	Load	Spalling	Shagging action	Abrasion	Remarks
Blast furnace	Lining	High-heat-duty fireclay brick, chrome cement	2200°F. (1205°C.)	15 to 20 lb. per sq. in.	None	Not severe	Important	Bottom part of furnace where highest temperature prevails is made of water-cooled cast iron. Density is main requirement of refractories
	Bottom	High-heat-duty and intermediate-heat-duty fireclay brick	2000°F. (1095°C.)	Unimportant	None	Important	Moderate	
	Side walls and end walls above metal line	High-heat-duty and intermediate-heat-duty fireclay brick	2000°F. (1095°C.)	10 lb. per sq. in., max.	Temperature change during charging, spalling slight	Important	Moderate	
	Side walls and end walls at and below metal line	Fireclay brick, magnesite brick, high-alumina brick	2000°F. (1095°C.)	10 lb. per sq. in., max.	Very slight	Very important	Moderate	
Drossing furnace	Roof	High-heat-duty and intermediate-heat-duty fireclay brick	2000°F. (1095°C.)	Arch stresses only	Moderate	Important	Very slight	
	Refining fire furnace box	High-heat-duty and intermediate-heat-duty fireclay brick, largely high-heat-duty brick	2000°F. (1095°C.)	10 to 15 lb. per sq. in.	Moderate	Moderate	Moderate	Conditions in firebox chamber vary depending upon whether oil, gas, or coal is used as fuel
	Bottom	High-heat-duty brick		Unimportant	None	Important	None	
	Side walls	Magnesite brick or high-alumina brick		Unimportant	Slight	Severe	None	
	Roof	Magnesite brick or high-alumina brick		Unimportant	Moderate	Moderate	None	

ories. Aluminum is melted, however, in the larger scale operations in small open-hearth furnaces holding about 20,000 lb. of metal. The temperatures are comparatively low, and the aluminum oxide is not very active but builds up on the walls and must be regularly sliced off. A good grade of dense fireclay brick accurately sized and giving thin joints has proved quite satisfactory, although in some cases the molten aluminum has a tendency to attack the brick, perhaps causing a thermite reaction with the iron oxide particles as suggested by Burrows.⁽³⁰⁾

7. Nickel.—Nickel is smelted in much the same way as copper, the detailed process depending a great deal on the type of ore available. The melting of nickel is often carried out in small open-hearth furnaces which are made almost completely of a dense fireclay brick, although super-duty fireclay and 50 per cent alumina bricks have been used with considerable success in some of the later furnaces.

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CHAPTER XXII

REFRACTORIES IN THE GENERATION OF POWER

1. Development of Boiler-furnace Refractories.—A study of the history of the development of steam generators, as given, for example, in "Steam,"⁽¹⁰⁾ will show a gradual but steady increase in the size of the unit, the steam pressure, the super-heat temperature, and the rating. The fuel, which in the early days was almost universally lump coal, is now often replaced with oil or gas—chiefly natural gas—or pulverized coal, changes that

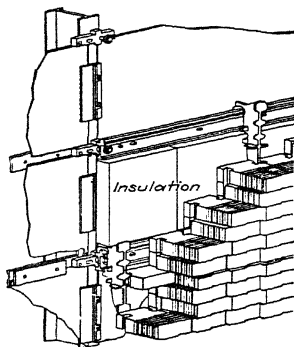
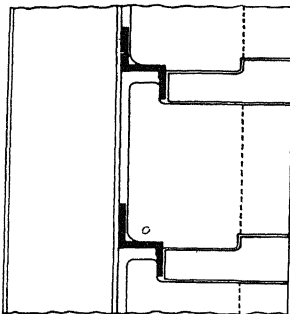


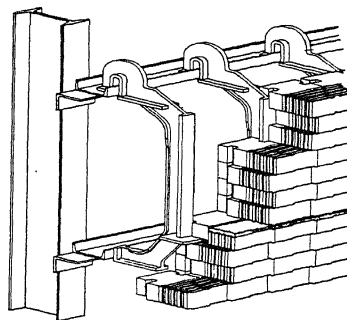
FIG. 354.—Sectionally supported walls. (a) Detrick insulated wall. (Courtesy of *Power magazine*.)

increase the temperature in the boiler furnace and, in the latter case, greatly accentuate the reaction of slag with the refractories. The boiler designer soon realized that the life of the refractories under such severe conditions was the limiting factor in the design of high-capacity steam-generating units,¹ a subject that has been discussed by Powell⁽¹⁾ and Bailey.⁽²⁾

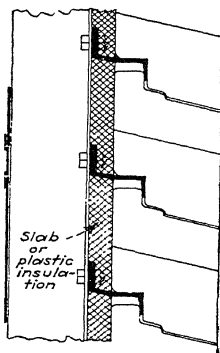
To improve this condition, certain modifications in the refractory were adopted, such as the suspended wall, sometimes with the air for combustion pulled through ducts back of the wall to



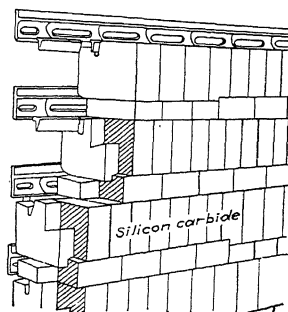
(b) Bigelow-Liptak air-cooled tile removed from furnace side.



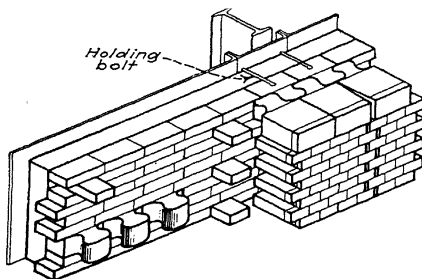
(c) Detrick air-cooled, panel construction.



(d) Bigelow-Liptak insulated wall tile removed from outside furnace.

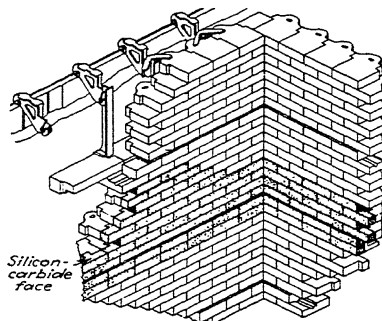


(e) Bigelow-Liptak wall faced with silicon carbide.

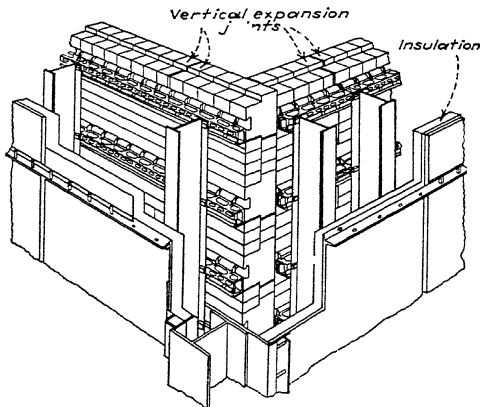


(f) Rust Engineering air-cooled wall without sectional support.

keep the face temperature down to reasonable limits. There are many patented constructions of this type; among well-known ones are the Detrick, Bigelow-Liptak, American Arch, and Reintjes, as shown in Fig. 354. Even this device did not prove



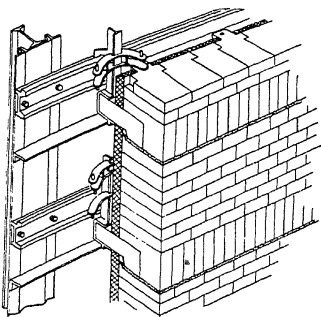
(g) American arch air-cooled, panel construction with silicon-carbide face.



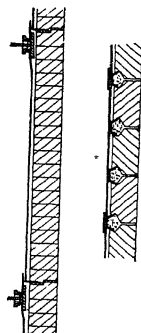
(h) Reintjes air-cooled, panel construction.

satisfactory for the larger units running at high ratings, especially when pulverized coal was used as a fuel. Under these conditions, it was found necessary to water-cool practically the whole furnace chamber, and therefore the steam-producing tube area has been partially transferred from the usual tube banks to the furnace

walls. It is well known, however, that with some low-volatile fuels, satisfactory combustion cannot be maintained if a large portion of the furnace area is kept at a low temperature; so the advantages of the water cooling were retained together with high surface temperature by the use of comparatively thin refractory facings in intimate contact with the water tubes. An important example of this practice is the Bailey stud-tube wall where chrome plastic is rammed between the water tubes and held in



(i) American Arch insulated wall, panel construction.



(j) Reintjes wall using insulating firebrick.

place by small studs welded to the tube surface. This construction will be more fully described later in the chapter.

2. **Boiler Furnace Using the Chain-grate Stoker.**—In Fig. 355 is shown a B & W cross drum boiler with a B & W chain-grate stoker. The bituminous coal in the hopper at the front of the furnace is carried slowly across the boiler furnace in a comparatively thin layer and at such a rate that combustion, carried out by air coming through the chain grate, is complete at the end of the furnace and ash and clinker fall down into the ash pit. The refractories used in a boiler of this type would consist of high-heat-duty brick in the boiler furnace itself and intermediate or low-duty brick in the upper parts of the setting. The front wall is largely of suspended construction, for which purpose special blocks are required. In a boiler furnace of this type, the slagging is not particularly severe, although there is a tendency for clinker to build up along the sides of the chain grate, and this must be sliced off occasionally, sometimes with a loss of the

refractory face. Side-wall water boxes or silicon carbide bricks, the latter often with air ventilation, are used in this zone, as the clinker has little tendency to stick to them.

The baffle running across the tube bank is, in present-day practice, usually made of a castable mix which is rammed in place

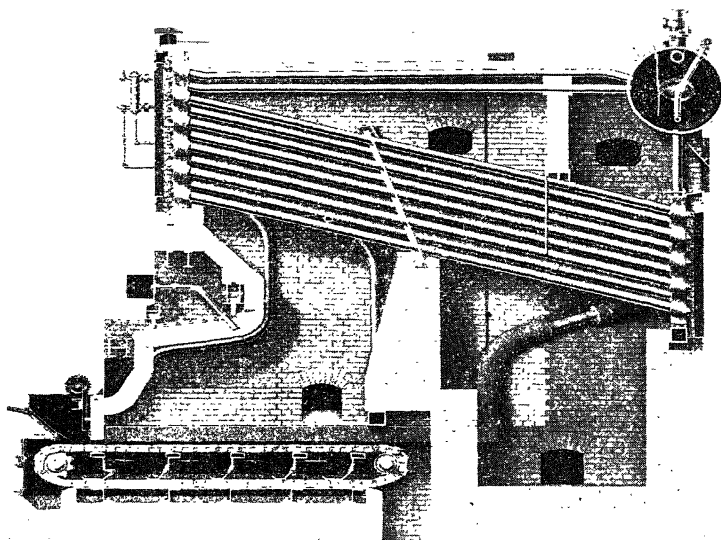


FIG. 355.—Babcock & Wilcox cross drum boiler with B & W chain-grate stoker.
(From "Steam," courtesy of Babcock & Wilcox Company.)

against a form; the temperature, of course, never attains a high value. In Fig. 355, the baffle is a tile construction in front of a cast-iron flame plate.

The life of the brickwork depends a great deal on the operation of the boiler, because frequent and rapid shutdowns will introduce conditions of spalling that may be quite severe. On the other hand, more or less steady operation will not subject the bricks to conditions that are at all drastic, unless high ratings are encountered with coal having low-fusing ash, in which case water cooling of the furnace is resorted to.

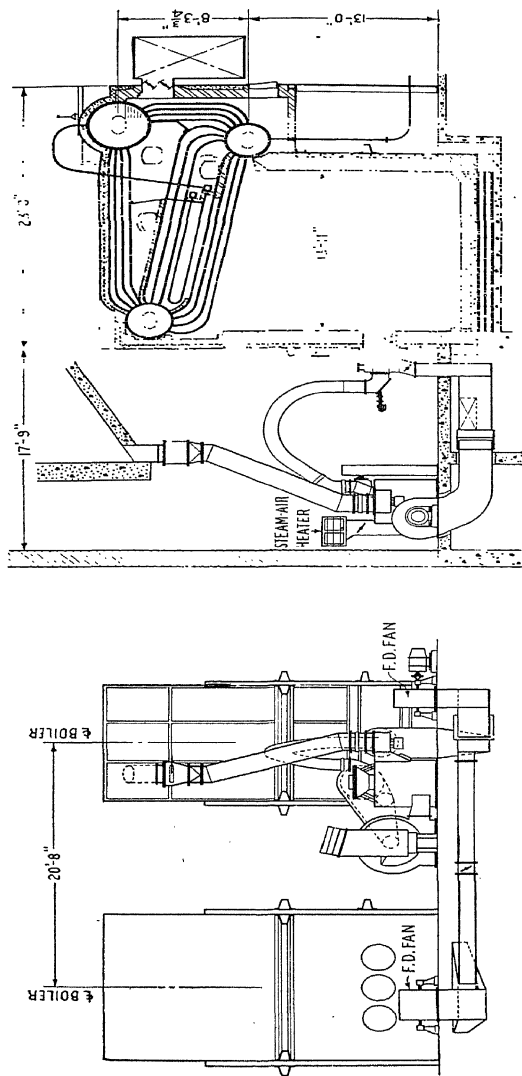


FIG. 356.—Babcock & Wilcox powdered-coal-fired boiler furnace. (Courtesy of Babcock & Wilcox Company.)

3. Boiler Furnace Using Pulverized Coal with Solid Walls.—

In Fig. 356 is shown a cross section of a boiler furnace for the

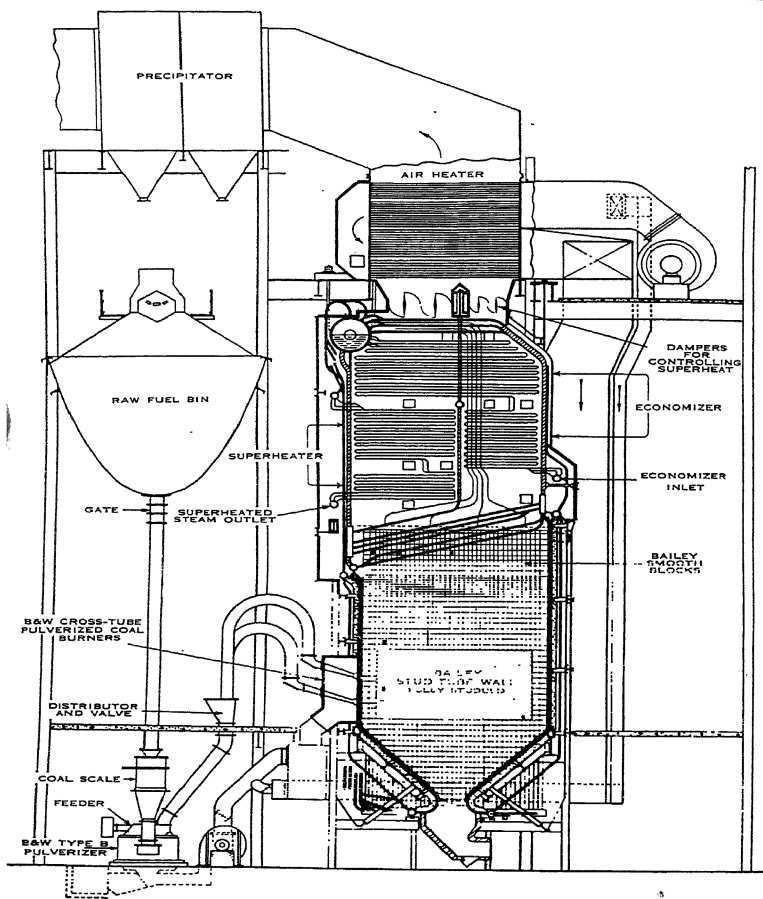


FIG. 357.—Babcock & Wilcox boiler for pulverized-coal fuel with water-cooled walls. (Courtesy of Babcock & Wilcox Company.)

use of pulverized coal where the rating is not excessive. The furnace chamber in this type of boiler is of large cubic capacity in

order that the coal may be thoroughly burned in the combustion chamber. The walls of the furnace are made of high-heat-duty, super-duty, or kaolin brick or sectionally supported air-cooled walls; while the bottom is an air-cooled fireclay refractory. The upper part of the boiler setting, where the temperature is comparatively low, is often constructed of insulating firebrick.

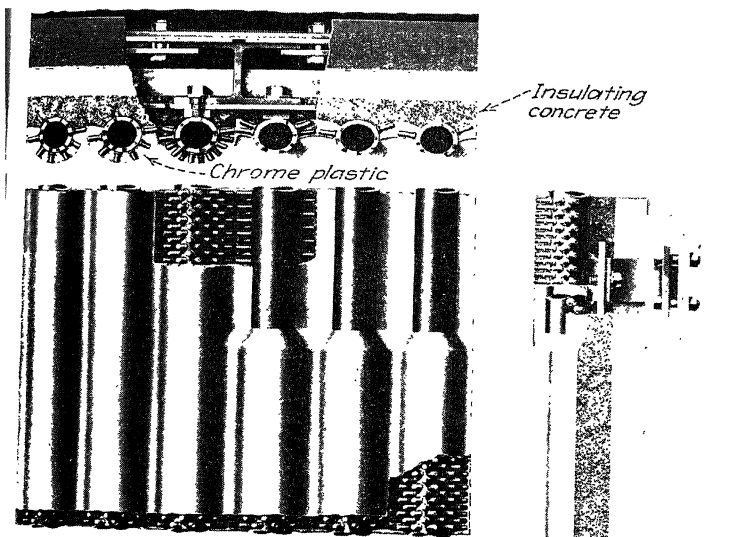


Fig. 358.—A section of Bailey stud-tube water-cooled furnace construction. (Courtesy of Babcock & Wilcox Company.)

Sections of the boiler furnace are often lined with a tile-and-tube construction where the tubes are set in formed tile. In the cooler portions, close-set tubes are sometimes used with lightweight castables.

In this type of boiler, the slagging action of the coal-ash slag may be comparatively severe where the coals have a low-melting ash. Also, there is some abrasion due to the high-velocity fly ash passing over the refractory surfaces.

4. High-capacity Pulverized Coal-fired Boiler.—In Fig. 357 is shown a large steam generator using pulverized coal for a fuel, in which the entire combustion chamber is water cooled. The

without repairs. Insulation is generally used outside the brick wall, which means that the refractories must attain a high mean temperature.

7. Waste-heat Boilers.—Waste-heat boilers are used in a great many industries for recovering heat in the flue gases from various types of industrial processes. Typical examples are the blast furnace and rotary cement kiln. The refractories used

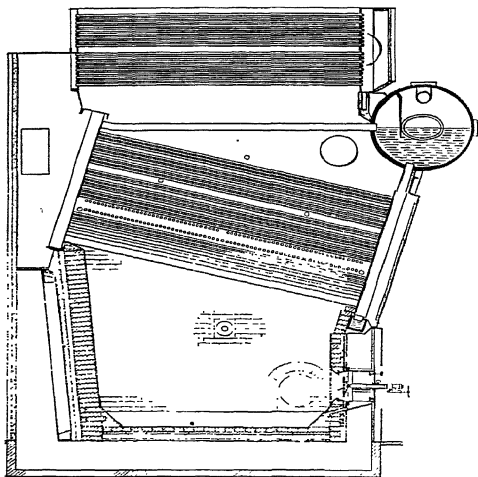
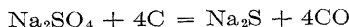


FIG. 361.—Babcock & Wilcox single-pass marine boiler. (*Courtesy of Babcock & Wilcox Company.*)

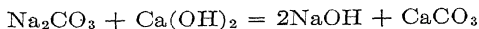
in the waste-heat boiler are always operated at comparatively low temperatures but, in general, are subjected to considerable abrasion, as most of the boilers operate under conditions where dust and ash are carried in the gases. For this reason, dense, intermediate-duty firebrick have been found quite satisfactory for these conditions.

8. Black-liquor Furnaces.—The economical operation of a modern sulfate or soda pulp mill necessitates the recovery of the chemical and heat values in the waste liquor. In the sulfate or kraft process, in which this recovery of chemicals and heat is most generally employed, the wood chips are digested with a hot alkali solution to remove the noncellulosic portion of the

wood, leaving the fibers for use in making paper—the cooking liquor in this process consisting of sodium sulfide, Na_2S , and sodium hydroxide, NaOH . The so-called “black liquor,” which is separated from the cellulosic fibers after the cooking or digesting has been performed, consists of a weak solution of the lignins separated from the wood in combination with the cooking chemicals, *e.g.*, sodium lignin sulfonates. In the more modern processes for the recovery of chemicals and heat from this liquor, the black liquor is evaporated in multiple-effect evaporators until it contains approximately 55 per cent solids and is then sprayed into a boiler furnace. The water in the concentrated liquor is quickly vaporized, and the resulting essentially dehydrated char, consisting of the carbonaceous material and inorganic salts, falls to the bottom of the furnace, where the carbonaceous material is burned by the admission of combustion air. As a result of this combustion, the inorganic salts in molten form are liberated and flow down through the bed of char, being discharged continuously from the furnace, whence they pass into a tank filled with water in which they are dissolved. The chemicals, on being liberated from the char as a result of combustion, are in the form of sodium sulfate, Na_2SO_4 , and sodium carbonate, Na_2CO_3 , the sodium carbonate being unchanged in the presence of the carbonaceous material, but the sodium sulphate being reduced to sodium sulfide in accordance with the formula



which is an endothermic reaction. This sodium sulfide is, as previously mentioned, a necessary constituent of the cooking liquor, and the sodium carbonate is subsequently causticized in accordance with the formula



The conditions existing in this furnace are extremely severe as far as action on the refractories is concerned, primarily in view of the eroding action of the fused sodium salts. In the earlier forms of recovery units, soapstone blocks were generally used as being the refractory best able to withstand the action of these molten sodium salts, but this material had a maximum life of only 10 to 12 months. In recent years, the Bailey partial stud-

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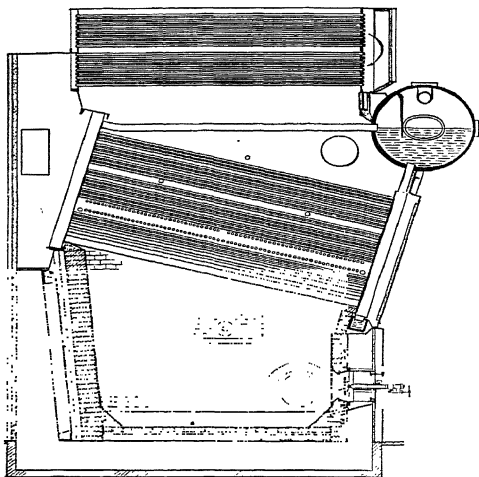
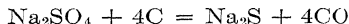


FIG. 361.—Babcock & Wilcox single-pass marine boiler. (*Courtesy of Babcock & Wilcox Company.*)

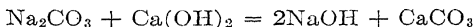
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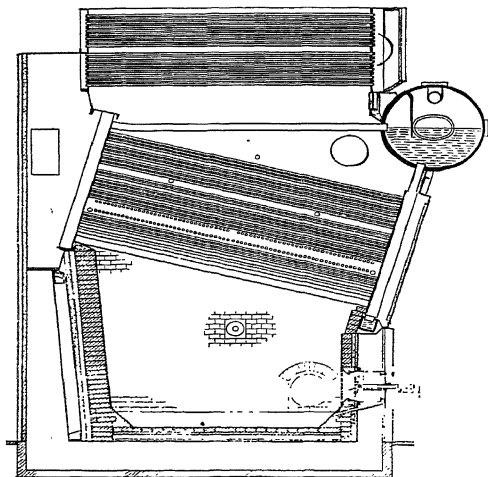
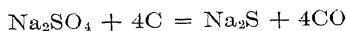


FIG. 361.—Babcock & Wilcox single-pass marine boiler. (*Courtesy of Babcock & Wilcox Company.*)

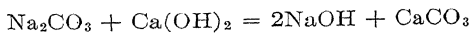
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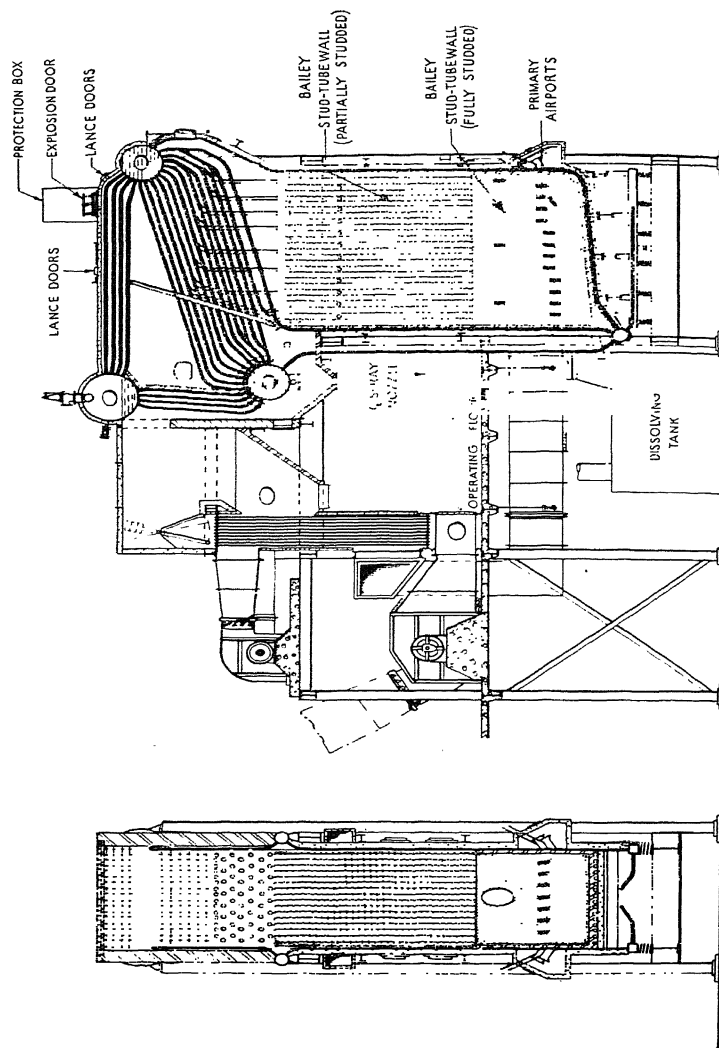


FIG. 362. Black-liquor furnace. (Courtesy of Babcock & Wilcox Company.)

tube wall with plastic chrome ore applied between the tubes has been employed to a considerable extent in furnaces of this kind with a high degree of success. The plastic chrome ore used in this instance, owing, undoubtedly, to the cooling action of the water tubes, is quite resistant to the action of soda, and the total life of this furnace construction has been materially increased, so that little if any work is necessary on the constructions over periods of from 4 to 6 years and even longer.

Figure 362 shows a section of a black-liquor recovery unit with the above-described construction of furnace, a large number of which have been installed in the kraft paper industry over the past few years.

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CHAPTER XXIII

USE OF REFRACTORIES IN MISCELLANEOUS INDUSTRIES

1. **Kilns.** *Periodic Kilns.*—The periodic kiln is used in the ceramic industry mainly for the firing of refractories and heavy clay products, with the use of coal as the principal fuel, although natural gas and oil are also used. A typical example of a round downdraft kiln of this type is shown in Fig. 169 of Chap. X. The maximum temperatures obtained in these kilns run from 1800° for some building brick to 2800° for silica brick.

The refractories used in the kiln are always fireclay brick, using low- or intermediate-duty brick for heavy-clay-products kilns and high-heat-duty or super-duty brick for the higher temperature kilns. Because of the fact that the kilns are heated and cooled fairly rapidly, silica brick would not be satisfactory.

Recently, a number of periodic kilns have been constructed, having a lining of insulating firebrick, that have shown distinct advantages over those lined with heavy types of brick. Kilns of this type have been used for firing common brick and also for firing glass-tank blocks with temperatures of 2600 to 2700°F. The main advantage in using the insulating firebrick is the great reduction in the heat stored in the walls and crown of the kiln. In many cases, this heat storage has been cut down to 25 per cent of the value for heavy bricks. This means, of course, a substantial saving in the fuel required for heating the kiln, a quicker turnover so that a kiln can produce more ware, and, perhaps as important, a more even temperature distribution over the kiln itself.

The refractories in periodic kilns generally have a comparatively long life, many kilns in operation having had only minor repairs in the last 15 or 20 years. The main source of trouble is spalling of the crown brick over the fireboxes, shrinking and softening of the bag walls, and slagging from the coal ash around the furnaces. With the use of forced draft and forced cooling of the kilns, the spalling tendencies are increased but, even under

these conditions, are not particularly severe. The use of insulating firebrick has not been studied for a sufficiently long period to give accurate information on the life; but from indications that we already have, it would seem that the life would compare favorably with the heavy brick.

The use of outer insulation on periodic kilns is increasing, especially on the crown. Although it is difficult to give any exact figures on fuel saving, the insulation does show a definite increase in economy and also enables a more uniform temperature to be maintained in the kiln. Of course, it may be necessary, when insulation is used on a high-temperature kiln, to employ a better grade of refractory to withstand the load at the higher mean temperature reached by the lining.

Continuous Kilns.—The tunnel kiln has been described in Chap. X. In general, the requirement for this type of kiln is a refractory lining that will give long, uninterrupted service at the required temperature level. There is little or no tendency to spall because the temperature at any one place is constant. Usually the side bricks must have good strength and abrasion resistance in case ware rubs against them during an accident. Therefore, in the modern kiln construction, low-heat-duty fireclay brick is used in the heating and cooling zones and intermediate- or high-heat-duty brick in the hot zones, although for some types of kiln running at high temperatures, super-duty fireclay or kaolin bricks are found useful.

The tunnel kiln, of course, must be very thoroughly insulated throughout its length; otherwise, a large amount of heat would be lost from the great amount of surface exposed. This is accomplished with insulating brick or blocks on the sides and a loose insulation on the top.

Some tunnel kilns have been constructed with a lining of insulating firebrick; but in this case, a low heat storage is not so important as with the periodic kiln and therefore the insulating firebrick does not have so big an advantage. However, from one point of view, this type of construction shows real economy, *i.e.*, in the kiln that must make a change in temperature to accommodate various types of ware fired. It is found that with the kiln lined with the insulating firebrick, a change in schedule can be made in a few hours with a minimum loss in ware during the turnover whereas with a heavy brick kiln, this

change of schedule may take a day or more and the loss in unproductive firing is much greater. Also, the lighter weight construction can use lighter steelwork and foundations.

Some tunnel kilns are indirect fired and have a muffle lining. This muffle should, of course, have a high thermal conductivity, good hot strength, and stability over long periods of time. Such muffles are usually made of clay-bonded silicon carbide or clay-bonded fused alumina. There are, however, certain temperature ranges in which the silicon carbide tends to oxidize, and care should be taken to follow the recommendations of the manufacturer of the refractory in its use.

Perhaps the portions of the kiln giving the most trouble are the car bottoms, because they are alternately heated and cooled each time that they pass through the kiln and, for this reason, suffer from thermal shock. There also is the difficulty of the setting sand, used in kilns firing refractories or heavy clay products, falling into the cracks between the car blocks when they are cool; and then as the car heats up, the blocks are forced apart and there is a gradual growth in the size of the car top until it eventually rubs on the kiln. For this reason, car bottoms are usually made of large shapes, and some manufacturers blow out the sand from the bottom of the car with compressed air each time that it comes out of the kiln. Considerable success has been had lately with car tops made of a lightweight castable mix which can be put on the car very cheaply by unskilled labor, a construction that seems to give good life in many installations.

Kiln Furniture.—In the last few years, a great deal of study has been made of the question of saggars, not only to increase their average life but also to reduce their wall thickness and weight for a higher efficiency. Many potteries are now purchasing saggars from refractory manufacturers rather than attempting to make their own. The old method of putting green saggars on top of the bungs filled with ware for the first firing has been largely superseded by prefiring the saggars at a somewhat higher temperature than would be used, with a consequent increase in strength. Although a few years ago the average life of the sagger was only 15 burns in a kiln, a life of twice that is now obtained, and instances of even greater life are often found. The recently developed loose-bottom sagger does much to reduce the heating and cooling stresses.

In manufacturing the sagger, care is taken in sizing the grog to a definite screen analysis and a more uniform structure is obtained in forming, often by the casting method. Although most of the saggings are still made of fireclay, special talc bodies have been tried as well as bodies containing alumina and silicon carbide. For glost work, the question of dusting is a very important one and must be considered along with the other characteristics of the body used.

The open setting of ware has been making great strides in almost all types of whiteware firing except in the hotel china field. Electrical porcelains, sanitary ware, and semivitreous table ware are now fired in open settings with a considerable increase in kiln capacity and a lower fuel cost per unit ware. The open-setting method consists in supporting a series of slabs on corner posts until the car is built up to the required height, as shown in Fig. 316, Chap. XVIII. Attempts are made, of course, to keep the thickness of the slab to a minimum and give the whole structure the greatest possible life. The furniture is usually made of clay-bonded silicon carbide, although clay-bonded used alumina and zircon refractories have been used. Many ingenious methods have been developed for supporting the slabs to minimize expansion stresses and still give a stable structure. There is still some difficulty with the slabs made of silicon carbide, in that they tend to increase in size, or grow, owing to gradual oxidation, each time that they go through the kiln. However, some of the more modern types of refractory have minimized this difficulty by surface coatings or other means to protect the silicon carbide from the air.

2. Glass Refractories. *General Types of Melting Furnace.*—Glass is melted in a number of types of furnace, one of them being the pot furnace where the glass is melted in open or closed pots, similar to a crucible, with the heat applied to the outside. This type of melting would be used for small batches of glass or glass necessitating very careful control, such as colored or optical glass. For larger production, small reverberatory furnaces called "day tanks" are used where the glass is melted in a hearth usually by producer gas using regenerators. The batch is melted down and worked out usually in a 24-hr. period; a new batch put in; and the process continued. For larger quantities of glass, the continuous tank is universally used, where raw

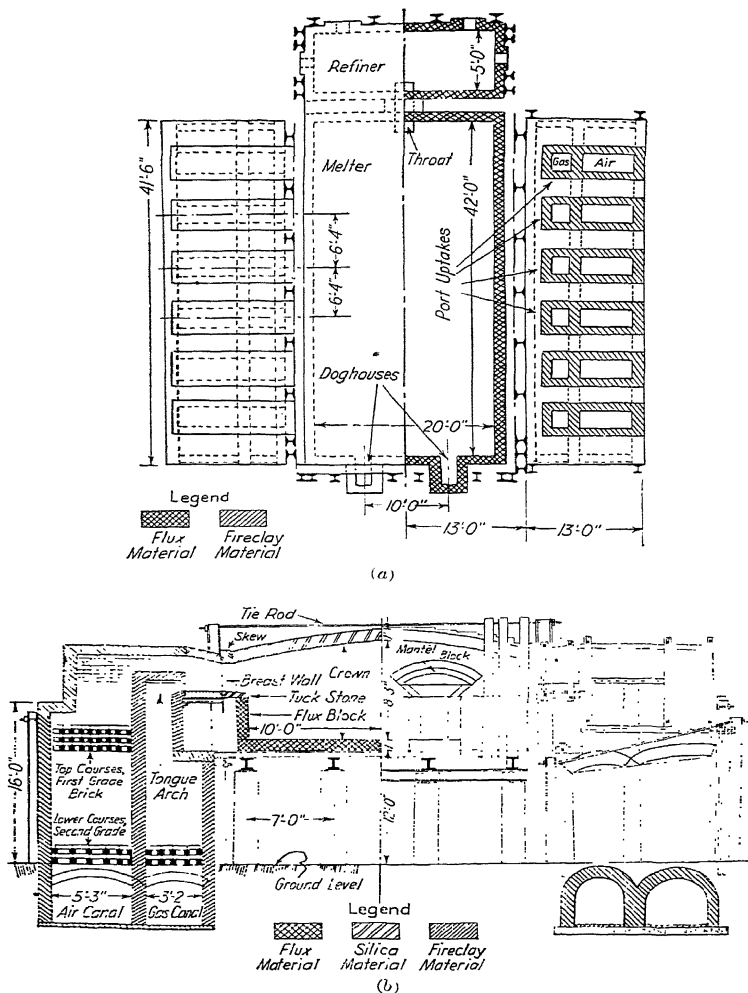


FIG. 363.—(a) Plan view of producer-fired regenerative-type glass furnace. (b) Half section on center line of first port, producer-fired regenerative-type glass furnace. (Courtesy of Owens-Illinois Glass Co., Toledo, Ohio, from "Manual of A.S.T.M. Standards on Refractory Materials.")

materials are fed in at a steady rate at one end and the glass drawn off continuously at the other end. These continuous tanks may be classified as bottle tanks for making containers and sheet-glass tanks for making window and plate glass by the continuous process.

A Typical Tank for Bottle Glass.—It will, perhaps, be best to take as an example of a continuous tank for making bottle glass the furnace shown in Fig. 363. This furnace consists of a melting chamber fired by producer gas preheated by a series of regenerators and a refining section connected to the melting section by a throat below the surface of the glass. This refining section receives no direct heat but is kept hot by conduction and radiation from the melting section. The temperature in the melting section is around 2600 to 2800°F.; whereas in the refining section, it is reduced to perhaps 2300°F. From the refining section, the glass is drawn out into forehearthers that have separate burners to maintain a uniform temperature.

The glass tank below the surface of the glass is composed of flux blocks which are generally a dense fireclay-grog-ganister mixture in comparatively large units in order to reduce the number of joints. A common size of these blocks would be 12 × 24 × 42 in., and they are usually ground accurately to size so that the joints are as thin as possible. No insulation is used around the bottom of the tank, as the higher mean temperature would permit more rapid solution of the blocks in the glass and also would tend to float the blocks out of the bottom. In fact air cooling is regularly used on the outside of the blocks.

The upper side walls and roof of the glass tank are constructed of silica brick, which are often used for the ports. Kaolin brick are finding increasing use in the upper parts of the tank.

In Table 103 is shown a classification of refractories used in the bottle-glass furnace together with their operating conditions. It is rather difficult to give any figures on the life of refractories in the glass-tank operation because it is so dependent on the type of glass, melting conditions, etc. It is usual, however, to run a continuous glass tank for six months to a year before the blocks wear so thin that a shutdown is necessary. The usual soda lime glass of window or bottle composition is not so active in attacking the blocks as the borosilicate glass or the opal glass.

TABLE 103.—CLASSIFICATION OF REFRACTORIES FOR GLASS FURNACE
(From "Manual of A.S.T.M. Standards on Refractory Materials")

Furnace part	Material	Temperature	Slugging action	Corrosion erosion	Abrasion	Spalling	Remarks
Melter:							
Bottom.....	Highly silicious hand-made, machine-made, or slip-cast block Molten cast block of high-alumina content	2500 to 2900°F. (1370 to 1595°C.)	Severe	Severe	Moderate	Slight	Spalling is of importance only during heating
Side.....							
Ends.....							
Refiner:							
Bottom.....	Same as melter	2350°F. (1290°C.)	Moderate	Moderate	Moderate	None	Same as melter
Side.....							
Ends.....							
Tank crown.....	Silica brick	Up to 2900°F. (1595°C.)	Moderate	Moderate	Severe in some furnaces	Important	
End walls.....	Silica brick	Up to 2900°F. (1595°C.)	Moderate	Severe in some furnaces	Severe in some furnaces		
Breast walls.....	Silica brick High-alumina brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port jambs.....	High-alumina brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port sills.....	High-alumina brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port wall sides.....	High-alumina brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port crowns.....	Fireclay brick	Up to 2700°F. (1489°C.)	Moderate	Moderate	Severe in some furnaces		
Port paving.....	Fireclay brick	Up to 2700°F. (1489°C.)	Severe	Severe	Severe in some furnaces		
Tongue arches.....	Silica brick	Up to 2900°F. (1595°C.)	Moderate	Moderate	Severe in some furnaces	Important	Spalling very important during heating

	action	erosion	Important	
Mantle block.....	2500°F. (1370°C.)	Severe	Important	
Regenerator wall crown.....	Up to 2000°F. (1090°C.)	Moderate	Moderate	
Checkers.....	Up to 2000°F. (1000°C.)	Severe	Severe in some furnaces	Silica and magnesite are sometimes used
Shadow wall.....	Up to 2800°F. (1540°C.)	Severe	Severe	
Tuckstones.....	Up to 2000°F. (1095°C.)	Severe	Severe	
Throat.....	2600°F. (1425°C.)	Severe	Severe	
Invert arches.....	Up to 2900°F. (1605°C.)	Severe	Severe	
Bridgwall covers.....	Up to 2800°F. (1540°C.)	Severe	Important	
Burner-block.....	Up to 2700°F. (1490°C.)	Severe	Important	
Skimmers.....	Up to 2800°F. (1425°C.)	Moderate	Important	
Feeder-tubes.....	Up to 2500°F. (1425°C.)	Moderate	Important	
Troughs.....	Up to 2400°F. (1315°C.)	Severe	Must have good transverse strength	
Plugs.....	Up to 2400°F. (1315°C.)	Severe	Must have good tensile strength	
Revolving tubes.....	Up to 2300°F. (1260°C.)	Moderate	Must have good shear strength	
Plunger needles.....	Up to 2300°F. (1260°C.)	Moderate	Important	Must have good tensile strength

The tendency is to use more and more insulation in the upper parts of the modern glass tank. It is now standard practice to insulate the regenerator chambers and often the uptakes and side port walls as well. Quite a number of insulated crowns are in use at the present time, but this construction is still viewed with suspicion by many operators.

Tank Blocks.—The demands on the flux blocks in the glass tank are particularly exacting, as the blocks are in contact continuously with the molten glass, and especially in portions where the movement of the glass is rapid, such as at the metal line and through the throat blocks, the attack is severe. Blocks for this service must have a low porosity, and particularly they must be free from flaws and laminations, which serve as an entering wedge for the glass erosion. Some believe that it is more important to have the pores all below a certain size than to have a minimum porosity, because apparently the surface tension of the glass will not permit it to enter pores below a critical size. Therefore, experience has shown that certain types of block, even with medium porosity, give good results if the pore size is very small. On the other hand, blocks with practically zero porosity made by casting the molten materials give good resistance to certain types of glass.

The chemical composition of the block does not seem to be so important as the physical characteristics. However, blocks made of mullite or alumina appear in general to have a resistance superior to those made of fireclay mixtures. Certain types of refractory, *e.g.*, chromite, that would be quite resistant to the glass cannot, of course, be used because of the color imparted to the glass.

Glass Pots.—The glass pot for melting glass is made of a carefully prepared fireclay-and-grog mixture with particular care to get a homogeneous structure. This is accomplished in modern practice by slip casting the pot in one piece from a high-density slip carefully deflocculated to give sufficient fluidity for pouring. The pot must have sufficient mechanical strength and resistance to creep at high temperatures so that the heavy load of glass will be supported without failure of the refractory. Here again it is difficult to give any definite figures on the life of the pot because it depends so much on the batch melted, the method of heating, and the type of fuel. However, pots often last for

10 to 20 melts before failure. In the manufacture of optical glass, the pot is used only once, because the batch and pot are cooled together and the pot is cracked away from the solidified glass.

3. Refractories in the Cement and Lime Industry. *Shaft Kilns for Lime Burning.*—All the lime was burned in shaft kilns in early days; and even now, the smaller plants use this type of kiln. As shown in Fig. 364, the kiln consists of a vertical shaft into which the raw material is fed at the top and the burned

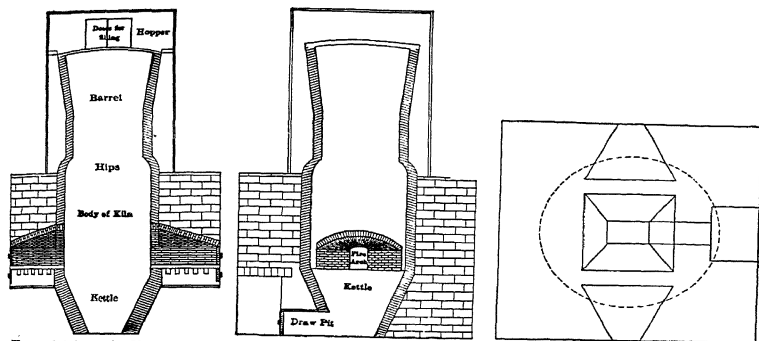


Fig. 364.—A lime kiln. (Reprinted by permission from "Cements, Limes and Plasters" by Eckel, John Wiley & Sons, Inc.)

material pulled out at the bottom. Coal-fired grates supply the hot gases necessary for the burning operation.

These kilns are lined with a dense fireclay brick to stand the abrasion of the moving charge; but recently, super-duty fireclay brick have been used successfully for high-temperature parts. Success has often been obtained by using silica brick around the eyes of the kiln.

Rotary kilns are now used for burning lime in the larger plants and, in construction, are very similar to kilns for Portland cement manufacture. The lining of these kilns is usually made of super-duty fireclay block or high-alumina block. For the hot zone, magnesite blocks have been successfully used with steel-sheet inserts between the individual blocks.

Kilns for the Manufacture of Portland Cement Clinker.—Portland cement is made from a mixture of limestone and clay,

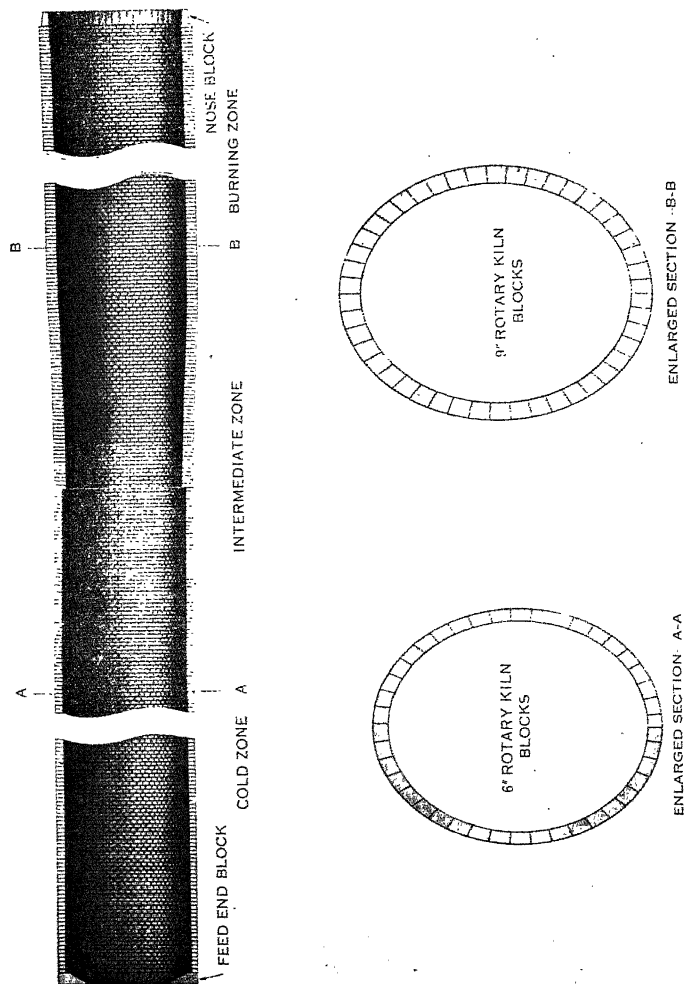


FIG. 305.—Rotary cement-kiln lining. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

ment rock, or slag, which will give approximately the following composition:

	Per Cent
SiO ₂	23
Fe ₂ O ₃	3
Al ₂ O ₃	8
CaO	63
MgO	2
SO ₃	1

Two general processes are in use: one in which the raw materials are dried, ground, and fed into the kiln as a powder. In the other, the materials are wet ground and fed into the kiln as a slurry. Most of the Portland cement manufacture in this country is carried out with the dry process; whereas in Europe, the wet process is favored. As far as the refractories are concerned, there is no great difference between the two methods.

TABLE 104.—USUAL SIZES OF ROTARY KILNS
(From "Portland Cement" by Meade)

Inside diameter, ft.	Length, ft.	Capacity, bbl. per day
6	60	200
7	100	430
8	125	625
9	150	1,100
9	175	1,430
9	200	1,775
10	175	
10	200	1,775
10	250	
11	250	

The rotary kiln lining, as shown in Fig. 365, is composed of special blocks usually of high-alumina material. In the hot end of the kiln, blocks are 9 in. thick; whereas in the cooler end, they are 6 in., and often insulation is used back of them in this portion. The temperature at the hot end of the kiln is rather high, reaching as much as 3000°F. (1650°C.), but there is little spalling. At the cool end of the kiln, the charge abrades the lining to some extent; and in the hot end, the clinker, which becomes soft, builds up a layer on the refractories and, under proper operating conditions,

protects them from slag attack and abrasion; *i.e.*, the most satisfactory refractory is one that will best hold this layer of clinker. Recently, kiln linings of chemically bonded magnesite brick have proved very satisfactory, as might be expected from the basic character of the clinker. In Table 104 are given the common sizes of rotary kilns for cement manufacture.

4. Gas Production. *By-product Coke Ovens.*—In this type of oven, the coking is carried out in a narrow chamber 16 to 22 in. wide, 10 to 12 ft. high, and 30 to 36 ft. long. The bituminous coal is fed in at the top until the chamber is full; then the coking

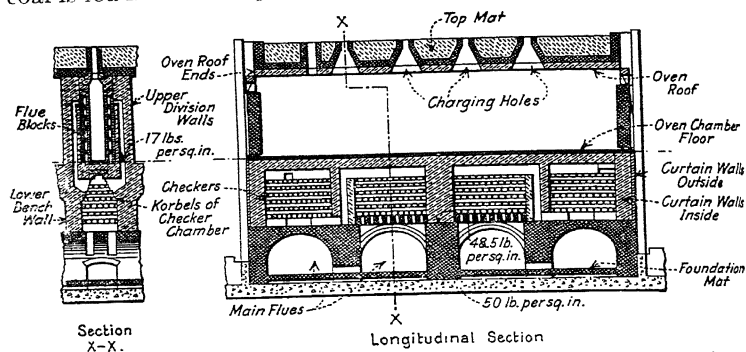


FIG. 366.—By-product coke oven. (Courtesy of American Refractories Institute.)

takes place by heat applied to the outer walls of this chamber. After the coking has been finished, the charge is pushed out of the chamber laterally and at once quenched. The gases escaping during the coking period (12 to 30 hr.) are collected in a large main and treated for removal of the by-products. A section of the Koppers type of by-product coke oven is shown in Fig. 366. It will be seen that the heating is regenerative, the gas usually being supplied by the coking process itself.

The walls of the coking chamber are comparatively thin to give low thermal resistance and therefore must have good mechanical strength. The refractory used is silica brick, the pores of which are more or less filled with coke after long operation. The bricks must, of course, be quite resistant to the abrasion of the entering and leaving charge, and there is a very rapid temperature change when the coal is dropped into the

red-hot oven chamber. Care must be taken not to allow the temperature to drop to the critical temperature for silica brick. Sometimes fireclay brick are used at the end of the ovens where spalling may occur. Table 105 gives a survey of the conditions of the refractory in this type of oven.

TABLE 105.—CLASSIFICATION OF REFRACTORIES FOR BY-PRODUCT COKE OVENS

From "Manual of A.S.T.M. Standards for Refractory Materials"

Part (See Fig. 369)	Material used	Temperature*	Slagging	Load as given for Koppers ovens lb. per sq. ft.	Load conditions in Semi- solway ovens	Abrasion	Spalling
Foundation mat	Fireclay brick	1830°F. (1000°C.), max.	No	25 to 30	Important	No	No
Hot flues	Silica brick and fireclay brick	1000°F. (540°C.) extraordinary 1300 to 1400°F. (705 to 760°C.)	No	16 to 20	Important	No	No
Lower bench walls	Silica brick	1830°F. (1000°C.), max.	No	18 to 20	Important	No	No
Chambers of checker chambers	Silica brick	1830 to 2550°F. (1000 to 1400°C.)	No	20 to 25	Important	No	No
Checkers	Fireclay brick and silica brick	1830 to 2730°F. (1000 to 1500°C.)	No	8 to 10	No	No	No
Chambers walls inside	Silica brick	1830 to 2550°F. (1000 to 1400°C.)	No		No	No	No
Chambers walls outside	Fireclay brick	390 to 1830°F. (200 to 1000°C.)	No		No	No	No
Upper division walls	Silica brick	1830 to 2550°F. (1000 to 1400°C.)	No	12 to 15	Important	No	No
End blocks	Silica brick	2190 to 2730°F. (1200 to 1500°C.)	No		Important	Important	No
Oven chamber floor	Fireclay brick	1830 to 2190°F. (1000 to 1200°C.)	No	3 to 6	No	Important	No
Oven roof	Silica brick	1830 to 2190°F. (1000 to 1200°C.)	No	6 to 10	Important	No	No
Oven roof ends	Fireclay brick	1830 to 2190°F. (1000 to 1200°C.)	No	5 to 10	Important	No	No
Charging holes	Fireclay brick	1470 to 2190°F. (800 to 1200°C.)	No		No	Slight	No
Chambers blocks	Silica brick and fireclay brick	1830 to 2730°F. (1000 to 1500°C.)	No	15 to 20	No	Important	Important
Top mat	Fireclay brick	1110 to 1830°F. (600 to 1000°C.)	No	5 to 10	No	No	No

The equivalent centigrade temperatures given in parenthesis are to the nearest five degrees.

Water-gas Generation.—Gas produced in this manner takes place by the following process: A chamber filled with a bed of hot coal has air blown through it to increase its temperature and produce a gas of nitrogen, carbon dioxide, and carbon monoxide, which is burned in a second chamber called a "carburetor" partially filled with checker bricks, thus raising their temperature. Sometimes a second checkerwork is used as a preheater. The

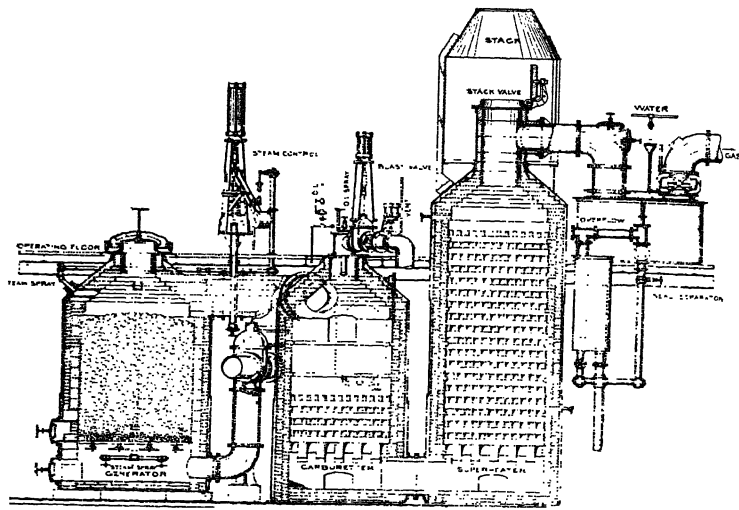


FIG. 367.—Carbureted water-gas machine, Champaign. (From C. W. Parmelee, A. E. R. Westman, and W. H. Pfeiffer, University of Illinois, Engineering Experiment Station.)

second part of the cycle consists in shutting off the air blast and passing steam through the hot coal which gives off hydrogen and carbon monoxide. This passes through the carburetor where it is preheated and enriched by the gas produced by spraying oil on to the hot checkers. As soon as the checkerwork is cooled to a predetermined value, the cycle is repeated. In Fig. 367 is shown a cross section of a typical water-gas generator operating on this principle. The refractories used are fireclay, as the temperature is not particularly high, but considerable resistance to spalling is necessary in the carburetor. Also, since the condi-

tions for the most part are highly reducing, the bricks must be capable of withstanding the disintegrating effects of hydrogen and carbon monoxide.

5. Incinerators.—Incinerators are used extensively for combustion of refuse and require refractories capable of standing sudden temperature changes, but they need never undergo very high temperatures. Therefore, a low-heat-duty brick with good spalling resistance is generally satisfactory.

6. Domestic Heating.—The increasing use of oil burners for domestic heating has made a really large field for refractories, even though the number of bricks in any one unit amounts to only a few dozen. The temperatures in this service are low, but the bricks must be quite resistant to spalling due to the intermittent action of the burner. In many types of installation, standard-size brick are used; but in a few cases, special shapes are assembled to reduce the labor cost.

The use of the insulating firebrick in this type of service has been increasing rapidly in the last few years because it permits a high temperature to be built up on the surface of the refractory immediately after the burner has started, so that efficient combustion takes place during the whole operation with less production of soot and lower consumption of oil. As the burner is only in operation for short periods of time, the immediate attainment of efficient combustion is very important. It has also been found that the sound-absorbing qualities of the porous insulating firebrick are very helpful in reducing the noise of the burner flame.

7. Paper-mill Refractories. *Sulfite Process.*—For sulfur- and pyrite-burning furnaces, high-heat-duty or super-duty fireclay brick are generally employed.

Soda and Sulfate Processes.—Refractories are required here for smelters, rotary incinerators, rotary and shaft kilns, and sludge recovery kilns. The slagging action is very severe in the smelting and recovery furnaces, as the soda salts are active fluxes. For the lower parts of these furnaces, soapstone or chrome brick are used, and dense high-heat fireclay brick are often employed in the upper portions. Black-liquor furnaces are discussed in Chap. XXII.

8. Enameling. *Cast Iron.*—Cast-iron enameling is generally carried out in recuperative-type muffle furnaces. The muffle, which is comparatively thin, is made of high-conductivity material, either silicon carbide or bonded alumina. The furnaces

are generally underfired, and the refractory requirements of the piers holding up the hearth are rather severe, as the brick are heated all the way through and must carry a heavy load. For this purpose, high-burned kaolin or mullite brick have been found very satisfactory. The walls of the furnace itself are generally made of high-heat-duty firebrick, and insulation is often used outside this. Since the doors of these furnaces must be quick acting, they are often lined with a lightweight castable mixture or with insulating firebrick that are tied into the door casing. This not only permits a rapid operation of the door but makes conditions much more comfortable for the men working around the mouth of the furnace.

~*Sheet-steel Enameling*.—In this type of furnace, a muffle construction is used; but in many of the modern continuous furnaces, very little refractory is required, as the heat is supplied by radiant metal tubes inside which the combustion takes place. The walls of the furnace outside these tubes can readily be constructed of insulating firebrick, since the requirements in the way of temperature, load, and spalling are not at all severe.

~*Enamel Fritting*.—Enamel frit is made in rotary oil-fired furnaces or in small tanks. In the former case, the lining is made from circle blocks of fireclay material. It is desirable to have the blocks as free from iron specks as possible. In the tank, the conditions are about the same as for glass melting, and therefore dense flux blocks are generally used.

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See Chap. X

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CHAPTER XXIV

BRICKWORK CONSTRUCTION

1. **Foundations.**—The foundations for kilns or furnaces are usually made of reinforced concrete to carry the usual engineering loads. These loads include not only the weight of the furnace itself and its charge but the thrust of the buckstay foot. As concrete loses considerable strength at temperatures above 400°C., it will be found necessary to protect the foundation from overheating if it is expected to maintain its full strength.

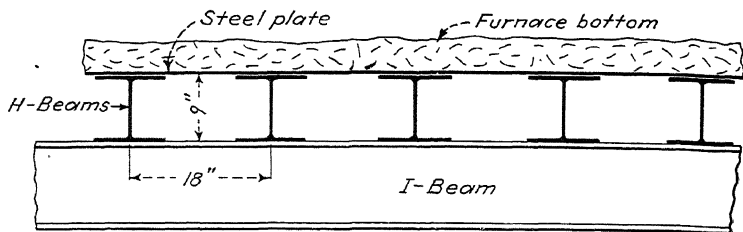


FIG. 368.—Supports for an open-hearth bottom.

In some cases, the foundation is poured with a lightweight concrete containing a quartz-free aggregate. A mixture of crushed brickbats and high-alumina cement is generally preferred, a material that can be heated to elevated temperatures without cracking or entirely losing its strength, although it cannot be depended upon to support any concentrated loads. When reinforcing is used in foundations subjected to heat, the expansion characteristics of the high-temperature concrete and the reinforcing rods should be investigated to prevent a differential expansion from cracking the foundation.

In certain types of furnace, the bottom is supported directly on the steelwork. For example, the open-hearth furnace, a section of which is shown in Fig. 368, has the bottom on a steel plate which is supported by a series of H beams, thereby providing ventilation as well as a rigid support. The glass-tank bottom, as shown in Fig. 369, has the flux blocks supported directly on

H beams, which permits the underside of the blocks to be air cooled.

2. Floors and Hearths. *Insulation.*—The floor or hearth of a furnace is usually insulated from the concrete foundation, both

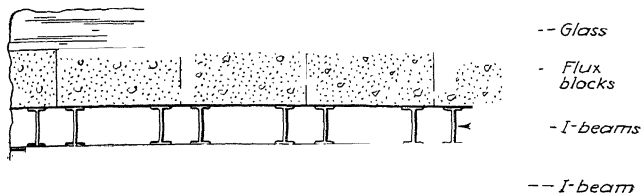


FIG. 369.—Construction of the bottom of a glass tank.

to conserve fuel and to prevent overheating of the foundation. The insulation is often accomplished by putting down a layer of hollow tile on top of the concrete foundation. In other cases, discarded steel boiler tubes are set in the upper surface of the concrete foundation, a few inches apart, to allow ventilation. Another method uses a layer of cinders tamped over the concrete foundation, on top of which are laid several courses of firebrick. In the smaller furnaces, two or three courses of insulating brick may be laid on the concrete and then heavy brick placed on top of them. Many furnace designers do not appreciate the large amount of heat that may be lost through the foundations if the insulation is not well taken care of.

Shapes and Bonds.—Most of the hearth structures are laid up with standard-size brick, a common type of construction being shown in Fig. 370. In some cases, however, larger blocks are used in the hearth to minimize the number of joints and to make larger units for reducing the tendency to float. In the case of the blast furnace, hearth blocks $18 \times 9 \times 4\frac{1}{2}$ in. are generally used. Sometimes these bottoms are keyed in to prevent floating. In the case of glass tanks, the bottom is made of large flux blocks often 24 by 48 in. across the face. Here again, the purpose is to minimize the joints and prevent the bottom from floating.

Expansion Joints.—It is just as important to have expansion joints in the hearth as in the walls, because failure to take care of this expansion will force out the base of the furnace and bend the buckstays or cause buckling of the bottom. The expansion

joints may be put in the hearth, as shown in Fig. 370, although expansion joints directly under the walls are not considered good practice by some designers. The amount of expansion to be left is considered more fully under the section on walls.

Monolithic Construction.—Many types of furnace hearth are constructed of a monolithic slab. The material may be magnesite grain as in the open-hearth furnace, chrome plastic as in

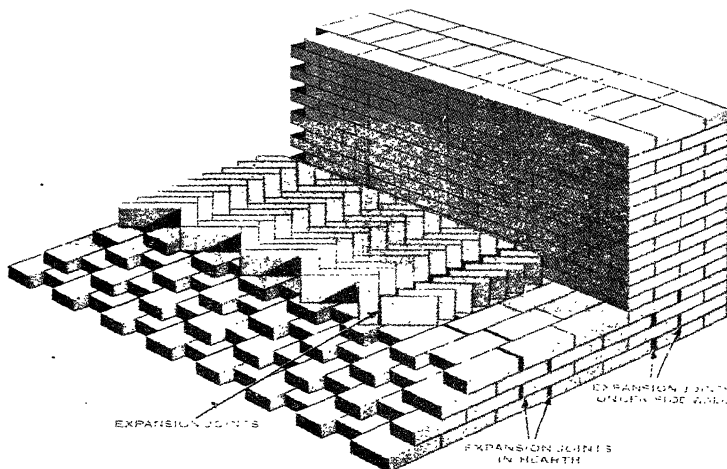


FIG. 370.—Method of construction sometimes used in heating furnace bottoms. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

the bottom of a powdered coal-fired boiler, or beach sand as in a malleable-iron furnace. There are two general methods of putting in the monolithic material. The first is to place it in dry, perhaps with a little slag, and sinter it down in layers until a firm hearth is produced. The other method is to ram in the plastic mix, while it is wet, to a homogeneous structure, then dry it out, and fire it in place. Refractory concrete, made with either ordinary or lightweight aggregate, is used to form monolithic hearths, particularly for car-bottom furnaces and tunnel-kiln cars.

3. Walls.—The walls of a furnace are primarily for the purpose of retaining the heat in the working chamber. To be satis-

factory, however, they must be stable under the severe operating conditions encountered. Experience has shown that certain limiting factors must be understood before satisfactory construction of walls can be accomplished.

TABLE 106.—SAFE WALL HEIGHTS FOR UNANCHORED WALLS

Wall Thickness, In.	Maximum Height* of Wall without Anchors but Arch
	Supported on Top of Wall, Ft.
4½	3
9	7
13½	12
18	15

* When wall does not support arch, the safe height is decreased 20 per cent.

TABLE 107.—WALLS MADE OF ONE KIND OF BRICK
Number of Straight

Wall Thickness, In.	Brick per Sq. Ft.
2½	3.6
4½	6.4
9	12.8
13½	19.2
18	25.6
22½	32.0
27	38.4
36	51.2

Refractory Lining of a Composite Wall

9, fifth course tie.....	14
9, fourth course tie.....	14.4
4½, fourth course tie.....	8.0
4½, third course tie.....	8.5
4½, alternate header and stretcher.....	9.6
Alternate 9" and 13½" courses.....	16.0

Backing-up Insulation of a Compound Wall

9, fifth course tie.....	11.5
9, fourth course tie.....	11.2
4½, fourth course tie.....	4.8
4½, third course tie.....	4.26
4½, alternate header and stretcher.....	9.6
Alternate 9" and 13½" courses.....	16.0

Thickness.—The thickness of the wall depends a good deal on the conditions encountered. From the point of view of stability, the higher walls must be thicker, as shown in Table 106. On the other hand, if the wall is subjected to severe slag attack or spalling, extra thickness must be built into it to give it a reasonable amount of life. Table 107 gives the number of

brick required for various thicknesses of wall, both solid and composite, data that will be useful in brickwork estimating. Table 108 gives the weight of various types of refractory for computing wall weights.

TABLE 108.—WEIGHT OF REFRACTORIES

Material	Weight per Cubic Foot
Fireclay brick.....	120-140
Super-duty brick.....	130-150
High-alumina brick:	
50.....	125-135
60.....	130-140
70.....	140-150
Fused Al_2O_3	153-196
Kaolin brick.....	130-135
Silica brick.....	100-110
Magnesite brick:	
Burned.....	160-175
Chemical bonded.....	180-185
Chrome brick:	
Burned.....	180-190
Chemical bonded.....	180-195
Silicon carbide brick.....	136-158
Forsterite brick.....	150-160
Insulating firebrick:	
1600°F.....	19-30
2000°F.....	28-40
2300°F.....	30-45
2600°F.....	39-55
2800°F.....	40-60
Insulating brick.....	20-35
Lightweight, castable.....	55-80 (45-75 fired)
Fireclay plastic.....	120-130
Chrome plastic.....	175-200
Mortar, high temperature.....	90-120
Mortar, chrome.....	125
1 cu. ft. of firebrick requires.....	seventeen 9-in. straights
1 cu. ft. of red brick requires.....	21 std. brick
1,000 firebrick closely packed occupy	60 cu. ft.

Bonds.—There are four ways of laying a standard brick, as indicated in Fig. 371. Nine-inch walls of one material are usually laid with all headers or with alternate header and stretcher courses. The rowlock courses are used for changing the height of the course, for sills and for some floors but are not often used in wall construction with refractories. The soldier courses are not particularly stable and would not be used where they are

expected to carry any amount of load. In building the thicker types of wall, it is necessary to bond the different layers together into a strong unit. Typical methods of bonding are shown in Fig. 372 for walls of different thickness. It should be noted that at the end of a wall, it is better to break the joint with a $6\frac{3}{4}$ -in. brick, referred to as a large 9-in. straight, rather than with a soap, as this construction gives much greater stability.

With composite walls, *e.g.*, a combination of heavy brick and insulating firebrick, it is necessary to tie one layer into the other.

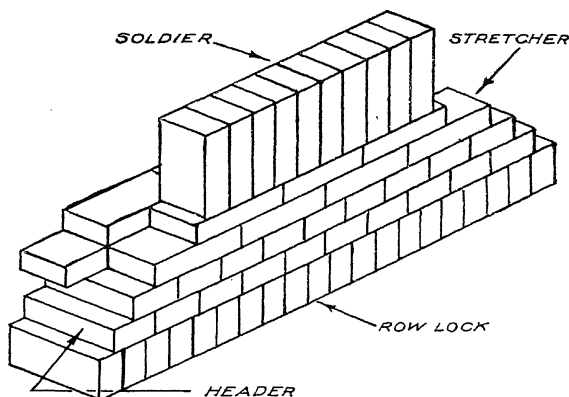


Fig. 371.—Methods of laying brick.

The general rule is that the tie should be made of the stronger layer, as it is less apt to break off. A number of methods of tying composite walls are shown in Fig. 373. In many cases, the tie brick can be made with soaps rather than straights when using an insulating-firebrick lining, which reduces the heat conductivity of the whole.

Many types of furnace construction are carried out with bricks larger than the 9-in. size for more rapid laying of the brick or for more solid structures. The 3-in. brick series is commonly used; and in some of the steel furnaces, still larger units are found useful. It should be noted that the dimensions of the standard brick are not ideal for the purpose of efficient laying. Strictly speaking, the thickness of the brick should be definitely related to the width and length, so that the brick could be tied

into the structure no matter in what position it was used. For example, if we consider the length of the brick 9 in. and use a $\frac{1}{16}$ -in. joint, the dimensions would be $9 \times 4\frac{15}{32} \times 2\frac{15}{16}$.

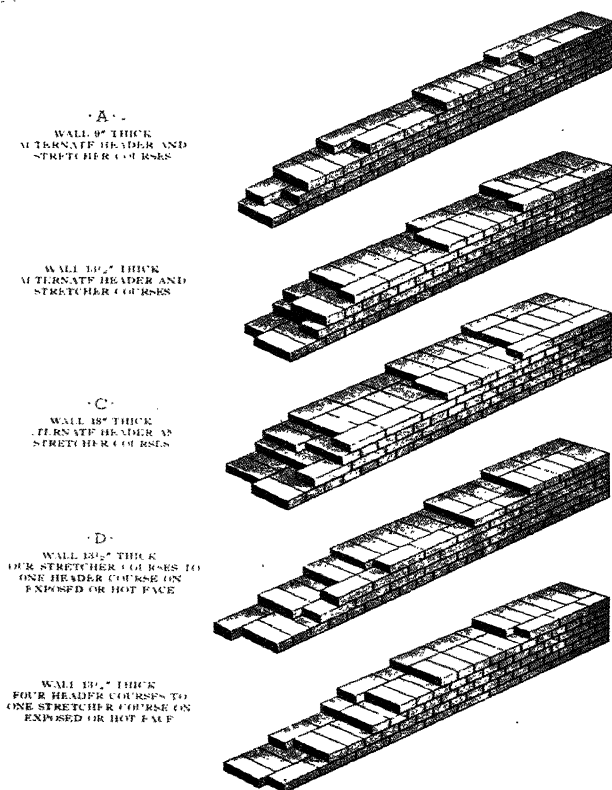
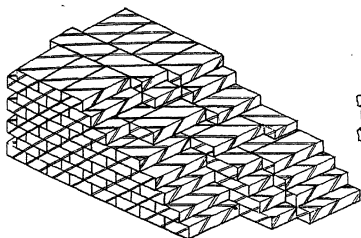
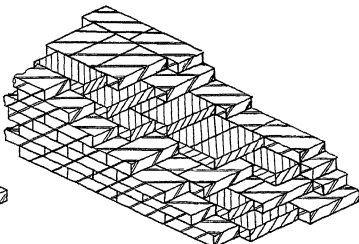


FIG. 372.—Bonding of walls built with standard 9-in. brick. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

Under these conditions, a rowlock course would equal two stretcher courses and one soldier course would correspond exactly to three stretcher courses. It will be seen that the 3-in. brick closely fulfills these conditions. ✓



BATTERY WALL - ONE GRADE



BATTERY WALL - TWO GRADES

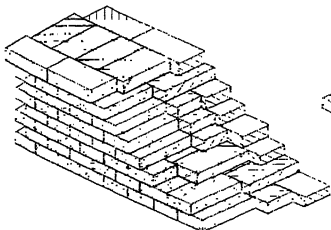
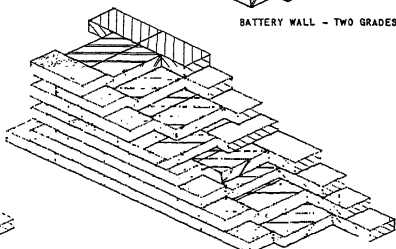
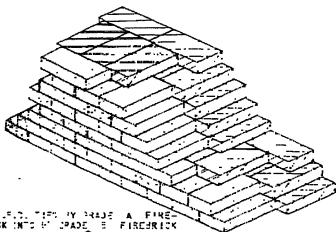
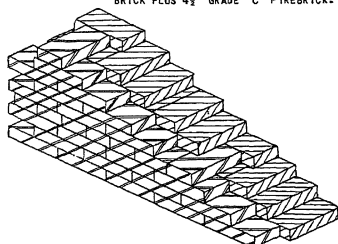
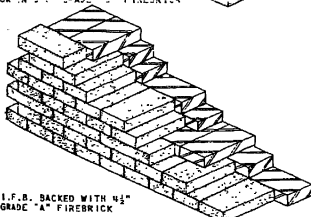
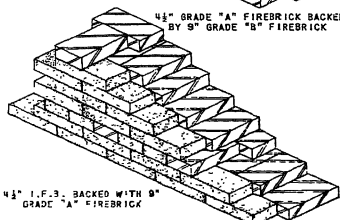
9" I.F.B. FACING TIED BY GRADE "A" FIRE-
BRICK INTO GRADE "C" FIREBRICK BACKING4 1/2" I.F.B. BACKED BY GRADE "A" FIRE-
BRICK PLUS 1 1/2" GRADE "C" FIREBRICK.9" I.F.B. FACING TIED BY GRADE "A" FIRE-
BRICK INTO GRADE "B" FIREBRICK4 1/2" GRADE "A" FIREBRICK BACKED
BY 9" GRADE "B" FIREBRICK9" I.F.B. BACKED WITH 4 1/2"
GRADE "A" FIREBRICK4 1/2" I.F.B. BACKED WITH 9"
GRADE "A" FIREBRICK

Fig. 373.—Method of bonding composite walls. (Courtesy of Babcock & Wilcox Company.)

Expansion Joints.—All except the smallest refractory structures must have allowance made for expansion on heating

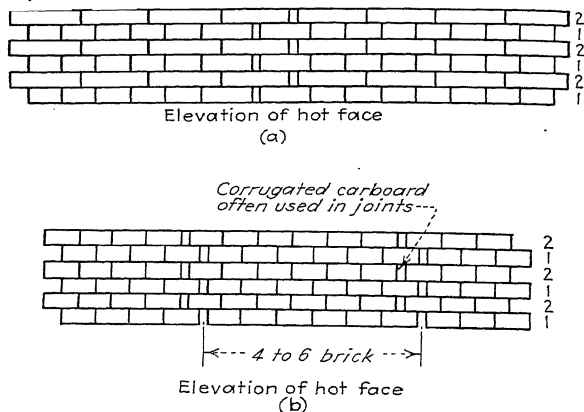


FIG. 374.—Expansion joints in walls. (a) $13\frac{1}{2}$ -in. wall, alternate header and stretcher construction. (b) Built of magnesite brick, 9-in. header construction. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

Considerable experience is necessary to know how many and what size expansion joints are to be used, but it is better to allow a little too much than not enough. An expansion joint

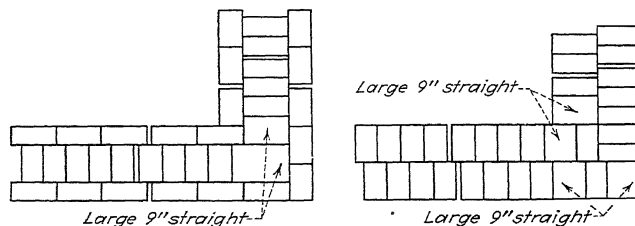


FIG. 375.—Double expansion joint in wall near corner. 18-in. wall, alternate courses showing header and stretcher construction. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

in a wall can be a straight vertical joint, or it can be a broken joint, as shown in Fig. 374. In other types of construction, particularly when using silica and magnesite bricks, the expansion

is taken care of by inserting a piece of cardboard in each vertical joint of the wall. This burns out and allows the individual bricks to expand freely.

When regular expansion joints are used, it is common in high-temperature furnaces to place them not more than 10 or 15 ft. apart, usually at the corners of the furnace first and then in

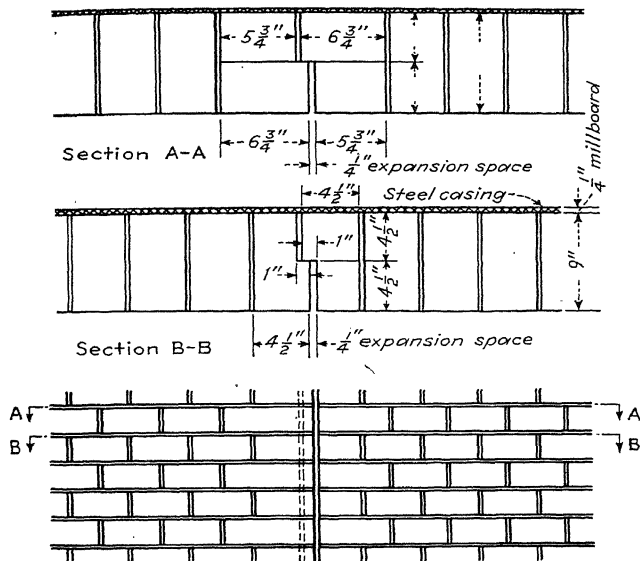


FIG. 376.—Expansion joint arrangement, 9-in. thick insulating firebrick wall. (Courtesy of Babcock & Wilcox Company.)

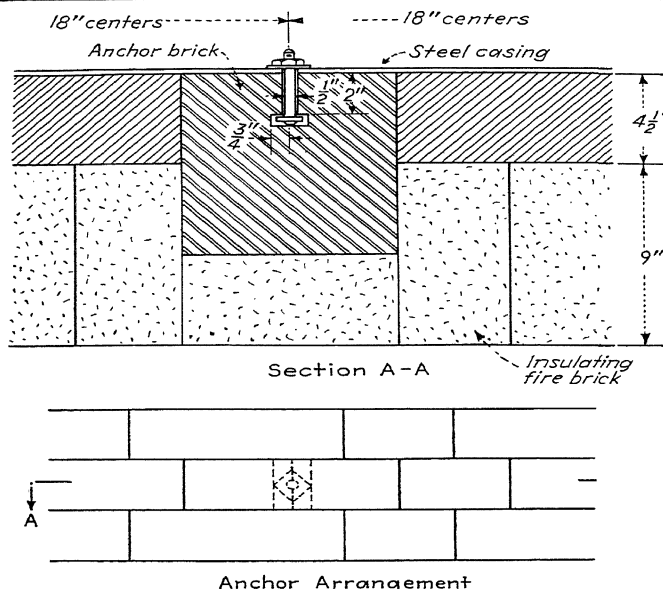
intermediate positions if necessary. In Fig. 375 are shown typical expansion joints near a corner. Figure 376 shows an expansion joint used with insulating firebrick inside a steel casing. If it is necessary to keep the expansion joints gastight, loosely packed asbestos rope or mineral wool can be used on the cooler face to seal them entirely. ✓

Horizontal expansion joints to allow for vertical expansion are sometimes required, as in sectionally supported walls and where the arch is supported independently of the walls. ✓

In Table 109 is given the width of expansion joints in inches per foot of wall for various types of refractory and at various temperatures.

TABLE 109.—WIDTH OF EXPANSION JOINTS IN INCHES PER FOOT OF WALL LENGTH

Type of refractory	Maximum hot-face temperature			
	1500	2000	2500	3000
Fireclay.....	$\frac{3}{64}$	$\frac{1}{16}$	$\frac{5}{64}$	$\frac{3}{32}$
Magnesite.....	$\frac{3}{32}$	$\frac{1}{8}$	$\frac{3}{16}$	$\frac{1}{4}$
Silica.....	$\frac{3}{16}$	$\frac{5}{32}$	$\frac{5}{32}$	$\frac{5}{32}$
Chrome.....	$\frac{1}{16}$	$\frac{5}{64}$	$\frac{5}{32}$	$\frac{5}{32}$
Silicon carbide.....	$\frac{1}{32}$	$\frac{3}{64}$	$\frac{1}{16}$	$\frac{5}{64}$
Kaolin.....	$\frac{1}{32}$	$\frac{3}{64}$	$\frac{1}{16}$	$\frac{5}{64}$



Anchor Arrangement

FIG. 377.—Anchor arrangement. (Courtesy of Babcock & Wilcox Company.)

Methods of Anchoring the Wall.—When very thin or high walls are used, they must be anchored at certain intervals to the casing

or steelwork to prevent buckling. The design of anchors has been greatly improved in the last few years and has thereby permitted the use of much thinner walls in many types of furnace. This anchoring is usually accomplished by a bolt fitting into a special brick. In Fig. 377 is shown one method of anchoring an insulating firebrick wall with a heavy brick tile. Figure 378

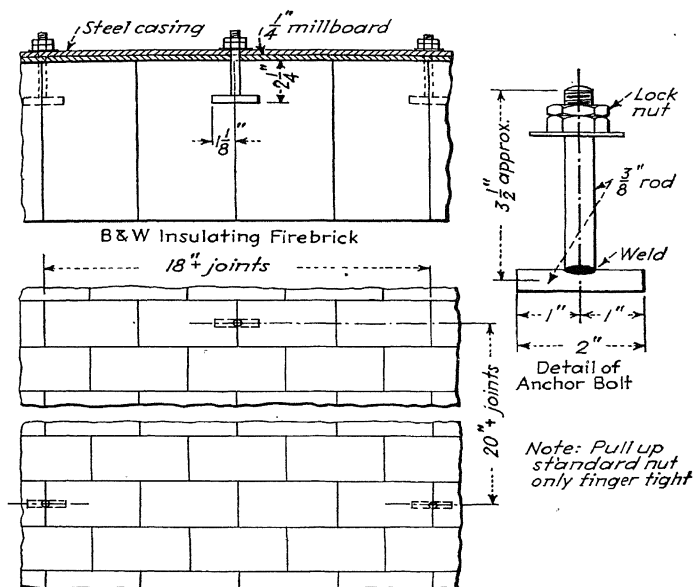


Fig. 378.—Method of holding insulating firebrick to casing. (Courtesy of Babcock & Wilcox Company.)

illustrates another method, where a T-headed bolt fitting into a slotted brick makes an excellent construction. ✓

The number of anchor bolts required for higher walls must be carefully worked out for efficiency and safety. The chart shown in Fig. 379 gives suggested vertical locations for anchor bolts in 9 in. thick walls.

✓ High walls, such as those used in boilers, even when 18 to 22½ in. thick must be anchored. This can be carried out by the use of special anchor tile as furnished by the various manufacturers. ✓

Insulation.—When insulation is applied to the outside of the wall, it may be tied in as shown in Fig. 373 or it may be placed between the refractory and a steel casing in the form of a block. In some types of construction, the outer face of the wall is made of red brick to protect the insulating material. This construction is stable, but it increases the heat storage of the wall, which is a disadvantage for intermittent operation, and also requires additional floor space. Many insulated furnaces simply have the corners protected with angle iron, and the face of the insulation is coated with a hard-face cement and possibly an

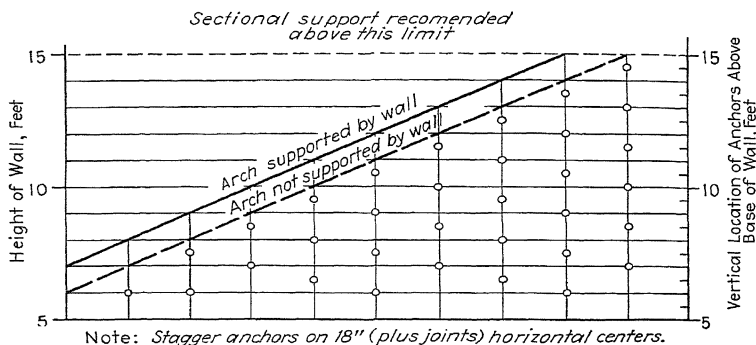


FIG. 379.—Stagger anchors on 18-in. (plus joints) horizontal centers. (Courtesy of Babcock & Wilcox Company.)

asphalt coating for waterproofing. Another method of protecting the insulation is to use a casing of approximately 10-gage sheet steel.

4. Doors, Ports, and Flues. Door Openings.—The door openings in most furnaces are among the most troublesome points in the structure, both because they mechanically weaken the wall and because the door frame must take considerable abuse from charging and hot gases. One of the first rules in door construction is to keep the width as small as possible compatible with access to the furnace. A typical door structure is shown in Fig. 380a, where a $4\frac{1}{2}$ -in. arch is thrown over the top of the opening and bonded into the wall. As the front 9-in. bricks are apt to be knocked loose, the sill of the door

should be made of a solid construction. This may be accomplished by using a rowlock course bonded with air-setting mortar or by using larger than 9-in. brick. Figure 380*b* shows a door opening, or port, of somewhat smaller size made up of special shapes, a construction that generally gives excellent service.

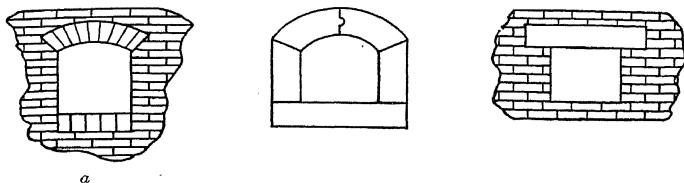


FIG. 380.—Door openings.

In Fig. 380*c* is shown a wall opening with a heavy tile across the top. This construction, although satisfactory for low-temperature work, is to be avoided for high-temperature furnaces, as the tile usually cracks in the center and the broken ends sag.

In the low-temperature structures, a steel door jamb is often placed outside the wall to protect the brickwork. This is welded

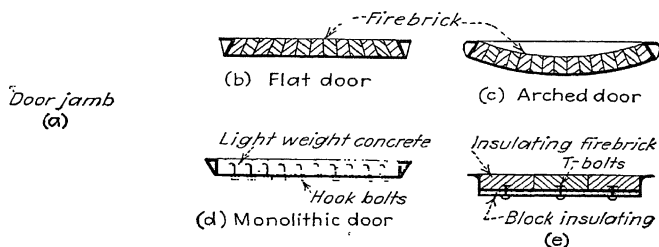


FIG. 381.—Door construction.

together from standard angle iron and makes a solid structure, as shown in Fig. 381*a*. For higher temperature furnaces, such as the open hearth, a water-cooled door jamb is generally used. It holds the brickwork in shape and resists to a considerable extent the abuse to which it is subjected from the charging machine.

Doors.—Doors on furnaces almost always slide in vertical ways with a counterweight to balance them approximately. The weight of the door should be kept as low as possible, in order to

reduce the cost of the supports and make the operation quicker. Two general types of door are the flat door and the arch door, as shown in Figs. 381*b* and 381*c*, where the shapes are locked into the door frame to prevent them from bowing in. Such a door will stand considerable mechanical abuse, but it is rather heavy and conducts much heat out of the furnace.

More recently, furnace doors have been lined with lightweight

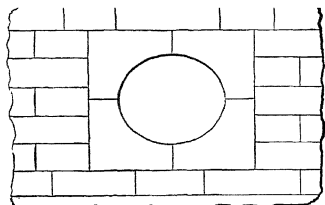


Fig. 382.—Burner tile set in wall.

concrete, held in place by hook bolts as shown in Fig. 381*d*. This construction is very simple to re-line, gives a light door, and has a comparatively low heat conductivity. Another construction for higher temperature use is shown in Fig. 381*e*, where the door is lined with insulating firebrick held into the door frame. This gives

a lightweight construction and one that is an excellent insulator; the latter is a factor of great importance to the comfort of the men working around the furnace.

Ports and Burner Openings.—Ports or openings in the furnace walls, when large, are constructed in the same way as described for the door openings. When the ports are smaller, a special shape often is set into the wall with the proper opening molded into it, or a number of shapes are fitted together to form the opening, as would be the case in burner tile as shown in Fig. 382. It is often found practical to form the port or opening out of plastic material which is rammed into place around the form in a rectangular opening in the brickwork. When properly made, such a construction often works out very satisfactorily and avoids the necessity of purchasing special shapes. Such plastic structures, however, are generally not so abrasion resisting as fired shapes and are not so satisfactory for extreme temperature conditions as preburned tile.

When walls are constructed of insulating firebrick, the ports or openings, when small, can often be cut directly in the wall after it has been finished. For larger openings, specially cut shapes can be used to advantage.

Flues and Ducts.—Flues and ducts for high-temperature use are lined with a refractory. The smaller sizes are usually

rectangular; and the larger ones circular, in which case arch or circle brick are generally employed. Where the moving gases in the duct do not carry a large amount of suspended particles, the ducts can well be lined with insulating firebrick, as a much thinner layer can be used because of its better insulating value. This, in turn, will allow a very much lighter lining which means lower cost of steelwork and supports. The cost of the duct can often be cut in half by the use of insulating firebrick.

Stacks.—Stacks for low-temperature furnaces are often of steel with a brick lining up to a sufficient distance to protect the steelwork. Insulating firebrick and lightweight concrete reinforced with wide-mesh, light-gage, expanded metal lath are frequently used for linings. For really high-temperature work, however, an all-brick stack is desirable such as that used for periodic kilns. Such a stack should have a firebrick lining that is free to expand and contract inside a stable wall such as is shown in Fig. 383.

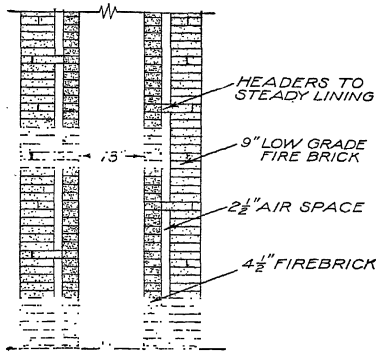


FIG. 383.—High-temperature stack.

5. Sprung Arches. Stresses and Shapes.—The circular arch, as generally employed, subtends an angle of 60 deg., which makes the radius of curvature equal to the span. However, there is no standardization in the ratio of span to rise of the arch, as in some cases a high arch is needed for combustion space and in others a very flat arch is desirable to force the flame down on the work. It should be noted that the circular arch in the higher forms becomes relatively unstable because of the fact that the line of thrust of the arch takes the form of an inverted catenary which departs more and more from the circular form as the height of the arch increases. Therefore, it has been found desirable always to employ the catenary form of arch when the ratio of rise to span is large. The curvature of the circular arch is usually expressed in inches of rise per foot of span.

- t = the thickness in feet.
 W = one-half weight of 1-ft. length of arch, lb.
 H = the horizontal thrust at skewback per foot of length, lb.
 R = the resultant thrust at skewback per foot of length, lb.
 l = the length of mean arc
 $\pi = 3.1416$
 d = the density of brick, lb. per cu. ft.

In Table 110 are given the important factors applying to circular arches of various heights. This table will be found useful for the quick calculation of the characteristics of arches.

TABLE 110

Inches rise per foot span	Central angle	Fraction of a com- plete circle	Weight factor, W_1	Horizontal- thrust factor, H_1	Resultant- thrust factor, R_1
1.000	37°51'	0.1051	1.02	2.90	3.07
1.250	47 04	0.1307	1.03	2.30	2.51
1.500	56 08	0.1560	1.04	1.87	2.13
1.608	60 00	0.1667	1.05	1.73	2.00
1.750	65 02	0.1807	1.06	1.57	1.86
2.000	73 44	0.2048	1.07	1.30	1.64
2.250	82 13	0.2284	1.09	1.15	1.52
2.500	90 29	0.2513	1.12	1.00	1.44
3.000	106 15	0.2952	1.16	0.76	1.25
6.000*	180 00	0.5000	1.57	0.00	1.00

* Unstable.

To find the weight of the roof multiply together the mean span, length, thickness (in feet), weight per cubic foot, and the factor W_1 .

To find the horizontal thrust on one skewback multiply the factor H_1 by one-half the total weight.

To find the resultant thrust on one skewback multiply the factor R_1 by one-half the total weight.

The temperature stresses in an arch are difficult to compute, but it may be said that they are greater in the flatter arches because a given expansion of the arch will produce a greater rise and more pinching of the tips of the bricks. To minimize this difficulty, especially with silica brick, tie bolts are often slacked off in a predetermined manner as the arch heats up, to keep the curvature constant. There is also another temperature stress, due to the temperature gradient through the arch itself, thus causing the tips of the bricks to expand more than the outer

face which puts an additional compression force on the inner surface. This latter effect can be minimized by using insulation on the outside of the arch.

The catenary shape has been found particularly satisfactory for some of the higher arches, thus allowing the side walls and

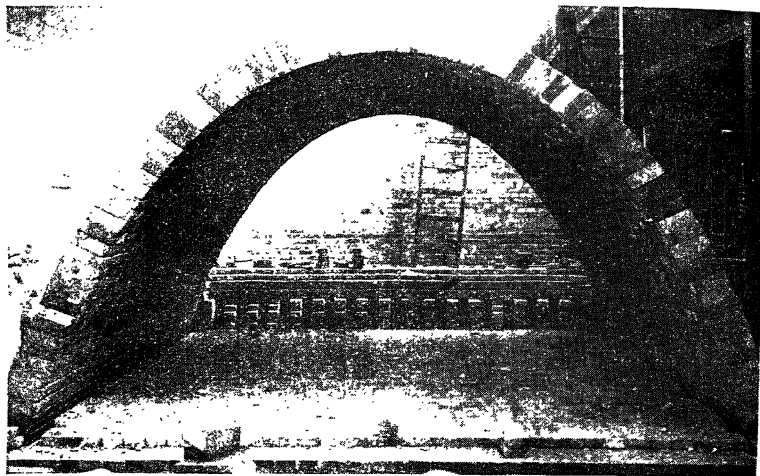


FIG. 385.—Catenary. (Courtesy of Babcock & Wilcox Company.)

crown to be one continuous curve with almost complete elimination of ironwork, as shown in Fig. 385. The calculation of the catenary can be carried out as follows.

The equation of the catenary as illustrated in Fig. 386 is

$$y = \frac{m}{2} (e^{\frac{x}{m}} + e^{-\frac{x}{m}})$$

or in hyperbolic functions

$$y = m \cosh \frac{x}{m}$$

The latter form is the most convenient to work with.

The slope angle at any point on the curve is given by

$$= \tan^{-1} \left(\sinh \frac{x}{m} \right)$$

The length of the curve between the apex and any point is

$$l = m \sinh \frac{x}{m}$$

The radius of curvature at any point is

$$r = \frac{y^2}{m}$$

The compression (or tension) at the apex is

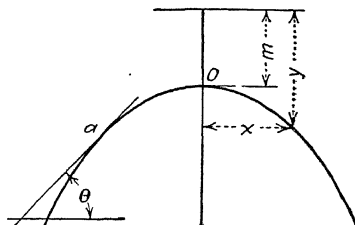


FIG. 386.—Catenary.

$$H = wm$$

where w = the weight per unit length of the curve

The following table shows the calculation of a typical high-catenary arch.

TABLE 111

x	$\frac{x}{m}$	$\cosh \frac{x}{m}$	y	$y - m$
0	0	1.000	19.0	0
5	0.263	1.035	19.7	7
10	0.527	1.142	21.7	2.6
15	0.789	1.328	25.2	6.2
20	1.054	1.609	30.6	11.6
25	1.317	2.000	38.0	19.0
30	1.579	2.528	48.1	29.1
35	1.841	3.231	61.4	42.4
40	2.108	4.177	79.5	60.5
42	2.210	4.613	88.0	69.0

$$m = 19$$

It will be found, in general, more convenient to lay out the catenary by hanging a sash-weight chain along a vertical surface in such a way as to pass through the three points representing the skewbacks and the apex. The chain thus hanging will form a perfect catenary, and the shape can be traced from this directly on the surface.

Arch Spans and Thicknesses.—It is a little difficult to give any hard-and-fast rules regarding the thickness and span of arches, as this ratio depends a great deal on the type of refractory, the

temperature of the furnace, and the operating conditions. In general, for heavy brick construction, a $4\frac{1}{2}$ -in. thickness would not be used for more than a 5-ft. span; a 9-in. arch would be used up to a 12-ft.; a $13\frac{1}{2}$ -in. arch up to 16 ft.; and an 18-in.



FIG. 387.—(a) Skewback built with standard 9-in. featheredge brick of the $2\frac{1}{2}$ -in. series. (b) Skewback built with standard 9-in. sideskew and endskew brick of the $2\frac{1}{2}$ -in. series. (Courtesy of J. S. McDowell and L. L. Gill, "Steel.")

arch up to 20 ft. However, there have been a number of successful operations at moderate temperatures with much wider arches than these. For example, a firebrick arch of 18-ft. span and 9-in. thickness has given an excellent life.

In the case of the insulating-firebrick construction; the thickness is seldom over 9 in.; but in moderate-temperature construc-

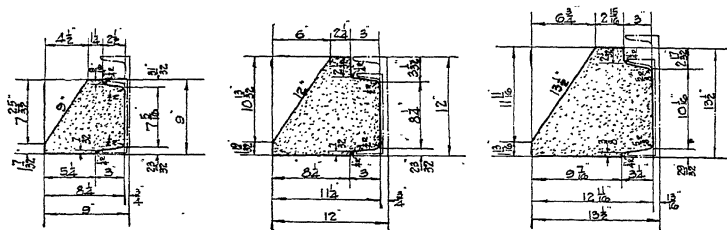


FIG. 388.—Skewback brick with cutouts for steel channel framework. (Courtesy of J. S. McDowell and L. L. Gill, "Steel.")

tion, the span often is as great as 15 ft.; and in one case, a 22-ft. arch has given excellent service.

Skewbacks.—The skewback must be made to give the proper angle for the ends of the arch, and it must have sufficient face to accommodate the thickness of the arch ring. Standard skewbacks are made with side skews and featheredge bricks as shown in Fig. 387, which accommodate $4\frac{1}{2}$ and $9\frac{1}{2}$ in. thick arches with rises of respectively $1\frac{1}{2}$ and $2\frac{5}{16}$ in. per ft. However,

special skewbacks can be readily obtained from most of the refractory manufacturers, as shown in Figs. 388, 389, and 390, for an arch of 60 deg. central angle. In the case of insulating firebrick, standard skewbacks can be made up as shown in Fig.

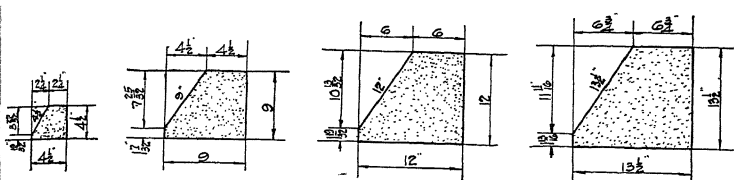


Fig. 389.—Sixty-degree skewbacks. Shape 60-4 1/2 is 9-in. thick; the others are 4 1/2-in. thick. (Courtesy of J. S. McDowell and L. L. Gill, "Steel.")

391 out of standard shapes, for arches having a 60 deg. central angle. In the case of the insulating firebrick, however, it is very easy to grind the skewbacks to any desired slope.

Methods of holding the skewback are shown in Fig. 392; but in all cases, the arch thrust should be well supported by the ironwork using either an angle section or a channel. As explained

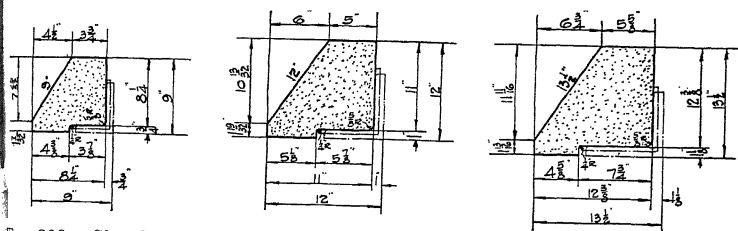


Fig. 390.—Skewback brick with cutouts for steel angle supporting framework. (Courtesy of J. S. McDowell and L. L. Gill, "Steel.")

previously, the arch can be supported on top of the wall or supported independently of the wall. The latter construction would be used where the life of the side walls is shorter than the arch, such as in a glass tank, in which case a replacement of the walls can be readily made without disturbing the arch. Also, in the case of heavy arches, less load is put on the side walls if the arch is separately supported. On the other hand, wall-supported arches tend to hold the top of the wall from bowing in.

is at a comparatively low temperature because of the small heat conductivity along the web. This condition produces a maximum of warping, which is often noticed in kiln construction, and thus allows a bowing of the walls.



Fig. 393.—Types of buckstay.

A simple section (B) or a H section (C) will be found thermally more efficient because it will maintain a much more uniform temperature over the section.

Bonding of the Arch.—Arches can be built up in a bonded construction, such as shown in Fig. 394, or in a separate ring

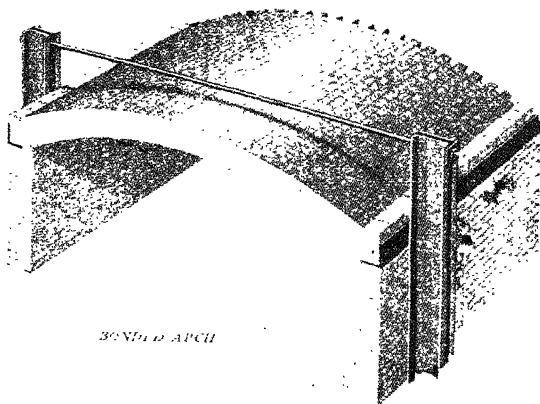


Fig. 394.—(From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

construction, such as shown in Fig. 395. The bonded construction has the advantage of giving a more stable structure in case of failure of one or two individual units. On the other hand, it requires a little more skill in laying in order to get a uniform load on all the bricks. In the separate ring arch, any one ring can be repaired without disturbing the others, which in some cases is a real advantage.

Special Arches.—There are many types of special arch, such as the rib arch in Fig. 396, often used in open-hearth-furnace crowns to give stability for long spans. The jack arch in Fig. 397 is made up of special shapes in order to give a flat lower

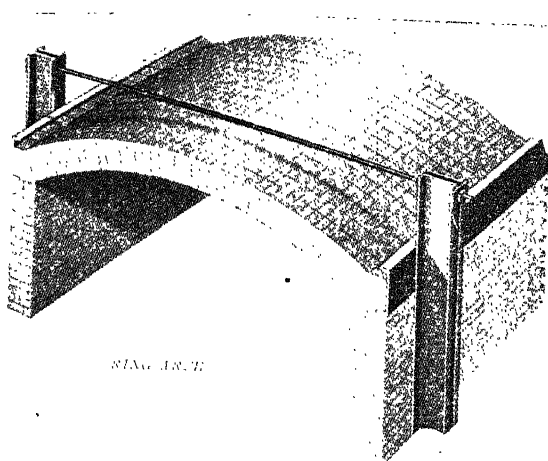


Fig. 395.—(From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

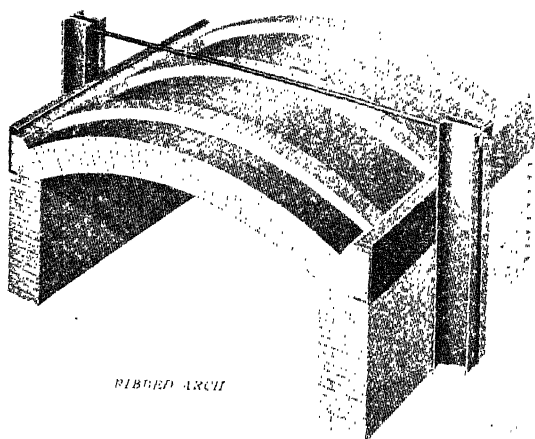


Fig. 396.—(From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.)

surface. This type of arch is often used in certain portions of tunnel kilns to conform closely to the charge.

The relieving arch shown in Fig. 398 is sometimes used to support the weight of an end wall and to take the load off the

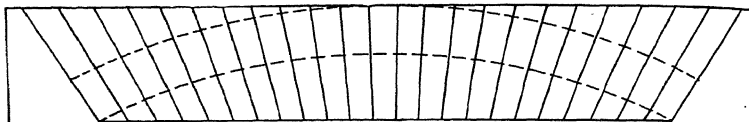


FIG. 397.—Jack arch. This type of arch is formed by special wedge shapes, which may be designed by first laying out a radial sprung arch of proper rise and thickness for the given span, then extending all brick shapes upward to the level of the upper crown surface and downward to the spring line. This arch is designed on a basis of $1\frac{1}{2}$ -in. rise per foot of span. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Co.)

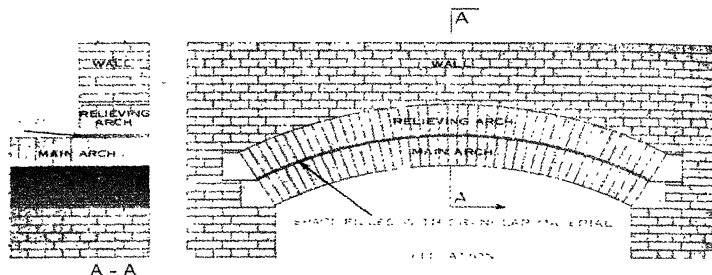


FIG. 398.—Use of relieving arch to support wall. (From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Co.)

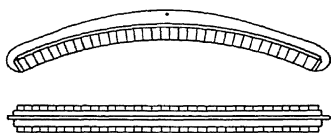


FIG. 399.—Bung arch.

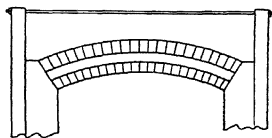


FIG. 400.—Double arch.

main arch. Relieving arches in modern construction are not used very extensively.

In Fig. 399 is shown a bung arch used in the malleable-iron industry. These arch rings are wedged tightly into a heavy iron frame so that they can be lifted off as individual units. Brick

TABLE 112.— $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ -IN. KEY BRICK*

Inside diameter	No. required to turn circle					
	No. 4 key	No. 3 key	No. 2 key	No. 1 key	Straight	Total
1'6"	26					26
2'0"	17	13				30
2'6"	9	25				34
3'0"		38				38
3'6"		29	13			42
4'0"		21	25			46
4'6"		13	38			51
5'0"		4	51			55
5'3"			57			57
5'6"			55	4		59
6'0"			50	13		63
6'6"			46	21		67
7'0"			42	30		72
7'6"			38	38		76
8'0"			34	46		80
8'6"			29	55		84
9'0"			25	63		88
9'6"			21	72		93
10'0"			17	80		97
10'6"			13	88		101
11'0"			9	96		105
11'6"			4	105		109
12'0"				113		113
12'6"				113	5	118
13'0"				113	9	122
13'6"				113	13	126
14'0"				113	17	130
14'6"				113	21	134
15'0"				113	26	139
15'6"				113	30	143
16'0"				113	34	147
16'6"				113	38	151
17'0"				113	42	155
17'6"				113	47	160
18'0"				113	51	164
18'6"				113	55	168
19'0"				113	59	172
19'6"				113	63	176
20'0"				113	68	181
20'6"				113	72	185
21'0"				113	76	189
21'6"				113	80	193
22'0"				113	84	197

TABLE 112.— $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ -IN. KEY BRICK.*—(Continued)

Inside diameter	No. required to turn circle					
	No. 4 key	No. 3 key	No. 2 key	No. 1 key	Straight	Total
22'6"				113	88	201
23'0"				113	93	206
23'6"				113	97	210
24'0"				113	101	214
24'6"				113	105	218
25'0"				113	109	222
25'6"				113	114	227
26'0"				113	118	231
26'6"				113	122	235
27'0"				113	126	239
27'6"				113	130	243
28'0"				113	135	248
28'6"				113	139	252
29'0"				113	143	256
29'6"				113	147	260
30'0"				113	151	264
30'6"				113	155	268
31'0"				113	160	273
31'6"				113	164	277
32'0"				113	168	281
32'6"				113	172	285
33'0"				113	176	289
33'6"				113	181	294
34'0"				113	185	298
34'6"				113	189	302
35'0"				113	193	306

* Applies also to $9 \times 4\frac{1}{2} \times 3$ -in. key brick.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

with good strength and spalling resistance are essential in this type of construction. In Fig. 400 is shown a double arch sometimes used in tunnel-kiln construction for preheating of the combustion air. This type of arch should never be used for high-temperature work because of the difficulty in making repairs on the inner arch.

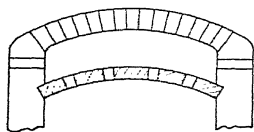


FIG. 401.—Perforated arch.

Figure 401 shows a perforated arch used in some types of over-fired furnace. As this arch is subjected to temperature on both

TABLE 113.— $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ -IN. WEDGE BRICK*

Inside diameter	No. required to turn circle			
	No. 2 wedge	No. 1 wedge	Straight	Total
2'3"	57			57
2'6"	51	10		61
3'0"	38	30		68
3'6"	25	51		76
4'0"	13	71		83
4'6"		91		91
5'0"		91	7	98
5'6"		91	15	106
6'0"		91	22	113
6'6"		91	30	121
7'0"		91	38	129
7'6"		91	45	136
8'0"		91	53	144
8'6"		91	60	151
9'0"		91	68	159
9'6"		91	75	166
10'0"		91	83	174
10'6"		91	90	181
11'0"		91	98	189
11'6"		91	105	196
12'0"		91	113	204
12'6"		91	121	212
13'0"		91	128	219
13'6"		91	136	227
14'0"		91	143	234
14'6"		91	151	242
15'0"		91	158	249
15'6"		91	166	257
16'0"		91	173	264
16'6"		91	181	272
17'0"		91	188	279
17'6"		91	196	287
18'0"		91	203	294
18'6"		91	211	302
19'0"		91	219	310
19'6"		91	226	317
20'0"		91	234	325
20'6"		91	241	332
21'0"		91	249	340
21'6"		91	256	347
22'0"		91	264	355

TABLE 110.—8 X 4½ X 2½-IN. WEDGE BRICK.*—(Continued)

Inside diameter	No. required to turn circle			
	No. 2 wedge	No. 1 wedge	Straight	Total
22'6"		91	271	362
23'0"		91	279	370
23'6"		91	286	377
24'0"		91	294	385
24'6"		91	301	392
25'0"		91	309	400
25'6"		91	317	408
26'0"		91	324	415
26'6"		91	332	423
27'0"		91	339	430
27'6"		91	347	438
28'0"		91	354	445
28'6"		91	362	453
29'0"		91	369	460
29'6"		91	377	468
30'0"		91	384	475
30'6"		91	392	483
31'0"		91	399	490
31'6"		91	407	498
32'0"		91	415	506
32'6"		91	422	513
33'0"		91	430	521
33'6"		91	437	528
34'0"		91	445	536
34'6"		91	452	543
35'0"		91	460	551
35'6"		91	467	558
36'0"		91	475	566
36'6"		91	482	573
37'0"		91	490	581
37'6"		91	498	589
38'0"		91	506	597
38'6"		91	513	604
39'0"		91	521	612
39'6"		91	528	619
40'0"		91	536	627
40'6"		91	543	634
41'0"		91	551	642
41'6"		91	558	649
42'0"		91	566	657
42'6"		91	573	664

TABLE 113.— $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ -IN. WEDGE BRICK.*—(Continued)

Inside diameter	No. required to turn circle			
	No. 2 wedge	No. 1 wedge	Straight	Total
43'0"		91	581	672
43'6"		91	589	680
44'0"		91	598	689
44'6"		91	605	696
45'0"		91	612	703
45'6"		91	620	711
46'0"		91	627	718
46'6"		91	635	726
47'0"		91	642	733
47'6"		91	650	741
48'0"		91	657	748
48'6"		91	665	756
49'0"		91	672	763
49'6"		91	680	771
50'0"		91	687	778
50'6"		91	695	786

* Applies also to $9 \times 6\frac{3}{4} \times 2\frac{1}{2}$ -in. wedges and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

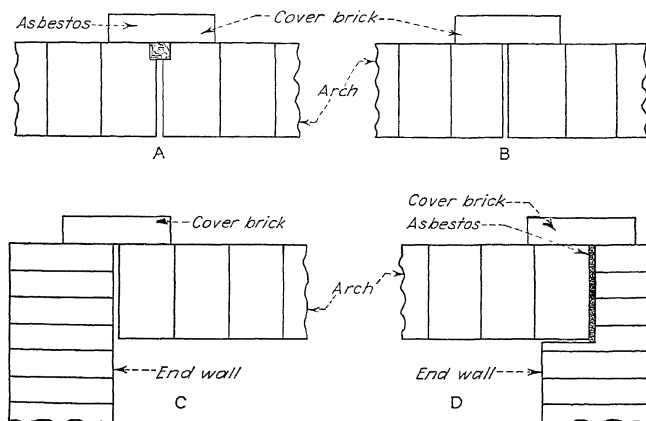


FIG. 402.—Construction of expansion joints. (Courtesy of the Babcock and Wilcox Company.)

TABLE 114.— $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ -IN. ARCH BRICK

Inside diameter	No. required to turn circle				
	No. 3 arch	No. 2 arch	No. 1 arch	Straight	Total
0'6"	19				19
1'0"	12	15			27
1'6"	4	30			34
1'9"		38			38
2'0"		34	8		42
2'6"		26	23		49
3'0"		19	38		57
3'6"		11	53		64
4'0"		4	68		72
4'3"			76		76
4'6"			76	4	80
5'0"			76	11	87
5'6"			76	19	95
6'0"			76	26	102
6'6"			76	34	110
7'0"			76	41	117
7'6"			76	49	125
8'0"			76	56	132
8'6"			76	64	140
9'0"			76	71	147
9'6"			76	79	155
10'0"			76	87	163
10'6"			76	94	170
11'0"			76	102	178
11'6"			76	109	185
12'0"			76	117	193
12'6"			76	124	200
13'0"			76	132	208
13'6"			76	139	215
14'0"			76	147	223
14'6"			76	154	230

TABLE 115.—9 × 4½ × 3-IN. WEDGE BRICK*

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
3'0"	57				57
3'6"	50	13			63
4'0"	44	26			70
4'6"	38	38			76
5'0"	32	50			82
5'6"	25	63			88
6'0"	19	76			95
6'6"	13	88			101
7'0"	6	101			107
7'6"		113			113
8'0"		107	13		120
8'6"		101	25		126
9'0"		94	38		132
9'6"		88	51		139
10'0"		82	63		145
10'6"		76	75		151
11'0"		69	88		157
11'6"		63	101		164
12'0"		57	113		170
12'6"		50	126		176
13'0"		44	139		183
13'6"		38	151		189
14'0"		32	163		195
14'6"		25	176		201
15'0"		19	189		208
15'6"		13	201		214
16'0"		6	214		220
16'6"			226		226
17'0"			226	7	233
17'6"			226	13	239
18'0"			226	19	245
18'6"			226	26	252
19'0"			226	32	258
19'6"			226	38	264
20'0"			226	45	271
20'6"			226	51	277
21'0"			226	57	283
21'6"			226	63	289
22'0"			226	70	296
22'6"			226	76	302

TABLE 115.—9 × 4½ × 3-IN. WEDGE BRICK.*—(Continued)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
23'0"			226	82	308
23'6"			226	89	315
24'0"			226	95	321
24'6"			226	101	327
25'0"			226	107	333
25'6"			226	114	340
26'0"			226	120	346
26'6"			226	126	352
27'0"			226	133	359
27'6"			226	139	365
28'0"			226	145	371
28'6"			226	152	378
29'0"			226	158	384
29'6"			226	164	390
30'0"			226	170	396
30'6"			226	176	402
31'0"			226	182	408
31'6"			226	189	415
32'0"			226	195	421
32'6"			226	201	427
33'0"			226	208	434
33'6"			226	214	440
34'0"			226	220	446
34'6"			226	227	453
35'0"			226	233	459
35'6"			226	239	465
36'0"			226	246	472
36'6"			226	252	478
37'0"			226	258	484
37'6"			226	264	490
38'0"			226	271	497
38'6"			226	277	503
39'0"			226	283	509
39'6"			226	289	515
40'0"			226	296	522
40'6"			226	302	528
41'0"			226	308	534
41'6"			226	315	541
42'0"			226	321	547
42'6"			226	327	553

TABLE 115.— $9 \times 4\frac{1}{2} \times 3$ -IN. WEDGE BRICK.*—(Continued)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
43'0"			226	334	560
43'6"			226	340	566
44'0"			226	346	572
44'6"			226	353	579
45'0"			226	359	585
45'6"					
46'0"			226	365	591
46'6"			226	372	598
46'6"			226	378	604
47'0"			226	384	610
47'6"			226	390	616
48'0"					
48'6"			226	397	623
49'0"			226	403	629
49'0"			226	409	635
49'6"			226	415	641
50'0"			226	421	647
50'6"			226	428	654

* Applies also to $9 \times 6\frac{3}{4} \times 3$ -in. wedges and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

sides, it must be made of material of high load-bearing capacity.

Expansion Joints.—The longitudinal expansion joints in the crown should, in general, be aligned with the expansion joints in the wall. It is often desirable to recess the end of the crown into the end wall as shown in Fig. 402, giving a labyrinth joint. Expansion joints coming in the center of the crown should be covered with a row of splits cemented in place, also shown in Fig. 402.

Brickwork Estimation for Sprung Arches.—The sprung arch is made up of various combinations of straights, arches, wedges, or keys. The simplest method of finding the number of shapes in a given arch ring consists in determining the count needed for a complete circle in Tables 112 to 125 and then multiplying the number of each shape by the fraction of the circle covered by the arch as given in the third column of Table 110.

For example, let us find the number and kind of bricks in a 9-in. arch with an 11-ft. span (S_i of Fig. 384) and a rise of 1.608 in. per ft. Here the inner radius is equal to 11 ft.; and from

TABLE 116.—9 × 6 × 3-IN. KEY BRICK*

Inside diameter	No. required to turn circle			
	No. 2 key	No. 1 key	Straight	Total
6'0"	48			48
6'6"	45	6		51
7'0"	41	13		54
7'6"	38	19		57
8'0"	34	26		60
8'6"	31	32		63
9'0"	27	39		66
9'6"	24	46		70
10'0"	21	52		73
10'6"	17	59		76
11'0"	13	66		79
11'6"	10	72		82
12'0"	6	79		85
12'6"	3	85		88
13'0"		91		91
13'6"		91	4	95
14'0"		91	7	98
14'6"		91	10	101
15'0"		91	13	104
15'6"		91	16	107
16'0"		91	19	110
16'6"		91	22	113
17'0"		91	26	117
17'6"		91	29	120
18'0"		91	32	123
18'6"		91	35	126
19'0"		91	38	129
19'6"		91	41	132
20'0"		91	44	135
20'6"		91	48	139
21'0"		91	51	142
21'6"		91	54	145
22'0"		91	57	148
22'6"		91	60	151
23'0"		91	63	154
23'6"		91	66	157
24'0"		91	70	161
24'6"		91	73	164
25'0"		91	76	167
25'6"		91	79	170
26'0"		91	82	173
26'6"		91	85	176
27'0"		91	88	179
27'6"		91	92	183
28'0"		91	95	186
28'6"		91	98	189
29'0"		91	101	192
29'6"		91	104	195
30'0"		91	107	198

* Applies also to 9 × 6 × 2½-in. keys and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 117.— $9 \times 4\frac{1}{2} \times 3$ -IN. ARCH BRICK

Inside diameter	No. required to turn circle				
	No. 3 arch	No. 2 arch	No. 1 arch	Straight	Total
1'6"	29				29
2'0"	22	13			35
2'6"	16	25			41
3'0"	10	38			48
3'6"	3	51			54
3'9"		57			57
4'0"		54	6		60
4'6"		47	19		66
5'0"		41	32		73
5'6"		35	44		79
6'0"		28	57		85
6'6"		22	70		92
7'0"		16	82		98
7'6"		10	94		104
8'0"		3	107		110
8'3"			113		113
8'6"			113	4	117
9'0"			113	10	123
9'6"			113	16	129
10'0"			113	22	135
10'6"			113	29	142
11'0"			113	35	148
11'6"			113	41	154
12'0"			113	48	161
12'6"			113	54	167
13'0"			113	60	173
13'6"			113	66	179
14'0"			113	73	186
14'6"			113	79	192

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick. smaller fractions are disregarded.

TABLE 118.—FLAT-BACK ARCH BRICK

Inside diameter	No. required to turn circle			
	No. 2 flat-back arch	No. 1 flat-back arch	Flat-back straight	Total
1'4"	26			26
1'6"	22	5		27
1'9"	16	14		30
2'0"	11	22		33
2'3"	5	30		35
2'6"		38		38
3'0 "		38	8	46
3'6"		38	15	53
4'0"		38	23	61
4'6"		38	30	68
5'0"		38	38	76
5'6"		38	45	83
6'0"		38	53	91
6'6"		38	60	98
7'0"		38	68	106
7'6"		38	75	113
8'0"		38	83	121
8'6"		38	91	129
9'0"		38	98	136
9'6"		38	106	144
10'0"		38	113	151
10'6"		38	121	159
11'0"		38	128	166
11'6"		38	136	174
12'0"		38	143	181
12'6"		38	151	189
13'0"		38	158	196

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 119.—12 × 6 × 3-IN. WEDGE BRICK

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
4'0"	76				76
4'6"	69	13			82
5'0"	63	25			88
5'6"	57	38			95
6'0"	51	50			101
6'6"	44	63			107
7'0"	38	75			113
7'6"	32	88			120
8'0"	25	101			126
8'6"	19	113			132
9'0"	13	126			139
9'6"	7	138			145
10'0"		151			151
10'6"		144	13		157
11'0"		139	25		164
11'6"		132	38		170
12'0"		126	50		176
12'6"		120	63		183
13'0"		113	76		189
13'6"		107	88		195
14'0"		101	100		201
14'6"		95	113		208
15'0"		88	126		214
15'6"		82	138		220
16'0"		76	151		227
16'6"		69	164		233
17'0"		63	176		239
17'6"		57	188		245
18'0"		51	201		252
18'6"		44	214		258
19'0"		38	226		264
19'6"		32	239		271
20'0"		25	252		277
20'6"		19	264		283
21'0"		13	276		289
21'6"		7	289		296
22'0"			302		302
22'6"			302	6	308
23'0"			302	13	315
23'6"			302	19	321
24'0"			302	25	327
24'6"			302	31	333
25'0"			302	38	340
25'6"			302	44	346
26'0"			302	50	352
26'6"			302	57	359
27'0"			302	63	365
27'6"			302	69	371
28'0"			302	75	377

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 120.—13½ × 6 × 3-IN. WEDGE BRICK

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
4'6"	85				85
5'0"	79	13			92
5'6"	73	25			98
6'0"	66	38			104
6'6"	60	50			110
7'0"	54	63			117
7'6"	47	76			123
8'0"	41	88			129
8'6"	35	100			135
9'0"	29	113			142
9'6"	22	126			148
10'0"	16	138			154
10'6"	10	151			161
11'0"	3	164			167
11'3"		170			170
11'6"		167	6		173
12'0"		160	19		179
12'6"		154	32		186
13'0"		148	44		192
13'6"		141	57		198
14'0"		135	70		205
14'6"		129	82		211
15'0"		123	94		217
15'6"		116	107		223
16'0"		110	120		230
16'6"		104	132		236
17'0"		97	145		242
17'6"		92	157		249
18'0"		85	170		255
18'6"		79	182		261
19'0"		72	195		267
19'6"		66	208		274
20'0"		60	220		280
20'6"		53	233		286
21'0"		48	245		293
21'6"		41	258		299
22'0"		35	270		305
22'6"		28	283		311
23'0"		22	296		318
23'6"		16	308		324

TABLE 120.— $13\frac{1}{2} \times 6 \times 3$ -IN. WEDGE BRICK.—(Continued)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
24'0"		9	321		330
24'6"		4	333		337
24'9"			340		340
25'0"			340	3	343
25'6"			340	9	349
26'0"			340	15	355
26'6"			340	22	362
27'0"			340	28	368
27'6"			340	34	374
28'0"			340	41	381
28'6"			340	47	387
29'0"			340	53	393
29'6"			340	59	399
30'0"			340	66	406
30'6"			340	72	412
31'0"			340	78	418
31'6"			340	85	425
32'0"			340	91	431
32'6"			340	97	437
33'0"			340	103	443
33'6"			340	110	450
34'0"			340	116	456
34'6"			340	122	462
35'0"			340	128	468
35'6"			340	135	475
36'0"			340	141	481
36'6"			340	147	487
37'0"			340	154	494
37'6"			340	160	500
38'0"			340	166	506
38'6"			340	172	512
39'0"			340	179	519
39'6"			340	185	525
40'0"			340	191	531
40'6"			340	198	538
41'0"			340	204	544
41'6"			340	210	550
42'0"			340	216	556
42'6"			340	223	563
43'0"			340	229	569

Table 113, it is seen that a circle of 22 ft. inside diameter requires 91 No. 1 wedges and 264 straights. Multiplying these figures

TABLE 120.—13½ × 6 × 3-IN. WEDGE BRICK.—(Continued)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
43'6"			340	235	575
44'0"			340	242	582
44'6"			340	248	588
45'0"			340	254	594
45'6"			340	260	600
46'0"			340	267	607
46'6"			340	273	613
47'0"			340	279	619
47'6"			340	286	626
48'0"			340	292	632
48'6"			340	298	638
49'0"			340	304	644
49'6"			340	311	651
50'0"			340	317	657
50'6"			340	323	663
51'0"			340	330	670
51'6"			340	336	676
52'0"			340	342	682
52'6"			340	348	688
53'0"			340	355	695
53'6"			340	361	701
54'0"			340	367	707
54'6"			340	374	714
55'0"			340	380	720
55'6"			340	386	726
56'0"			340	392	732
56'6"			340	399	739
57'0"			340	405	745
57'6"			340	411	751
58'0"			340	418	758
58'6"			340	424	764
59'0"			340	430	770
59'6"			340	436	776
60'0"			340	443	783

fractions are disregarded.

by the fraction of a circle 0.1667, the final count is 15 No. 1 wedges and 44 straights per ring. This calculation allows

TABLE 121.— $13\frac{1}{2} \times 6 \times 3$ -IN. KEY BRICK*

Inside diameter	No. required to turn circle			
	No. 2 key	No. 1 key	Straight	Total
6'0"	52	7		52
6'3"	48	16		55
7'0"	43	24		59
7'6"	38	32		62
8'0"	33			65
8'6"	28	40		68
9'0"	23	48		71
9'6"	18	56		74
10'0"	13	64		77
10'6"	8	73		81
11'0"	3	81		84
11'3"		85		85
11'6"		85	2	87
12'0"		85	5	90
12'6"		85	8	93
13'0"		85	11	96
13'6"		85	14	99
14'0"		85	18	103
14'6"		85	21	106
15'0"		85	24	109
15'6"		85	27	112
16'0"		85	30	115
16'6"		85	33	118
17'0"		85	36	121
17'6"		85	39	124
18'0"		85	43	128
18'6"		85	46	131
19'0"		85	49	134
19'6"		85	52	137
20'0"		85	55	140
20'6"		85	58	143
21'0"		85	61	146
21'6"		85	65	150
22'0"		85	68	153
22'6"		85	71	156
23'0"		85	74	159
23'6"		85	77	162
24'0"		85	80	165
24'6"		85	83	168
25'0"		85	87	172
25'6"		85	90	175
26'0"		85	93	178
26'6"		85	96	181
27'0"		85	99	184
27'6"		85	102	187
28'0"		85	105	190
28'6"		85	109	194
29'0"		85	112	197
29'6"		85	115	200
30'0"		85	118	203
30'6"		85	121	206
31'0"		85	124	209
31'6"		85	127	212
32'0"		85	131	216
32'6"		85	134	219
33'0"		85	137	222
33'6"		85	140	225
34'0"		85	143	228
34'6"		85	146	231
35'0"		85	149	234

* Applies also to $13\frac{1}{2} \times 6 \times 2\frac{1}{2}$ -in. bricks and straights.

* The fractional parts of a circle of a brick or more are counted as entire brick; other fractions are disregarded.

TABLE 122.—9-IN. CIRCLE BRICK

Inside diameter	No. required to turn circle					
	24-33	36-45	48-57	60-69	72-81	Total
2'0"	12					12
2'3"	9	4				13
2'6"	6	8				14
2'9"	3	12				15
3'0"		16				16
3'3"		12	5			17
3'6"		8	10			18
3'9"		4	15			19
4'0"			20			20
4'3"			16	5		21
4'6"			10	12		22
4'9"			4	19		23
5'0"				24		24
5'3"				17	9	26
5'6"				12	15	27
5'9"				6	22	28
6'0"					29	29
	72-81	84-93	96-105	108-117	120-129	
6'3"	21	9				30
6'6"	14	17				31
6'9"	7	25				32
7'0"		33				33
7'3"		23	11			34
7'6"		14	21			35
7'9"		5	31			36
8'0"			37			37
8'3"			25	13		38
8'6"			18	21		39
8'9"			10	30		40
9'0"				41		41
9'3"				34	8	42
9'6"				23	20	43
9'9"				13	31	44
10'0"					45	45

TABLE 123.—9-IN. CUPOLA BLOCKS

Inside diameter	No. required to turn circle							
	A	B	C	D	E	F	G	H
1'4"	9							
1'6"	6	4						
1'8"		11						
2'0"		6	6					
2'3"			13					
2'6"				14				
3'0"				6	10			
3'4"					18			
3'6"					14	4		
4'0"					5	15		
4'3"						21		
4'6"						14	8	
5'0"							24	
5'6"							12	15
6'0"								29
6'1"								29

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

nothing for joints that may average $\frac{1}{32}$ to $\frac{1}{16}$ in. for the modern dipped joint.

The arch can be computed for any case without the tables by finding the total number of bricks in the ring, which is the outer arc in inches divided by 2.5 or 3.0 in. The number of tapered brick is found by dividing the difference between the inner and outer arcs in inches by the taper of a single brick in inches.

When using insulating firebrick, it is often advisable to have them all ground with such a taper that the joints will all be radial. This construction, of course, makes the best type of arch.

Forms.—Steel forms are to be preferred for arch construction that is often rebuilt. On the other hand, wooden forms are less expensive and quite satisfactory for one job. The forms are usually lagged with 2- by 2-in. oak strips.

The form should be accurately placed, with wedges or jacks for lowering. The arch should be built up from both skewbacks simultaneously to meet at the apex. The keys should be care-

TABLE 124.—6-IN. CUPOLA BLOCKS AND 6-IN. ROTARY-KILN BLOCKS

Inside diameter	No. required to turn circle						
	30-42	36-48	42-54	48-60	54-66	60-72	66-78
2'6"	15						
2'9"	8	8					
3'0"		17					
3'3"		8	10				
3'6"			19				
3'9"			9	11			
4'0"				21			
4'3"				10	12		
4'6"					23		
4'9"					13	11	
5'0"						26	
5'3"						14	13
5'6"							28
	60-72	66-78	72-84	78-90	84-96	90-102	96-108
5'9"		16	13				
6'0"			30				
6'3"			18	13			
6'6"				32			
6'9"				19	14		
7'0"					34		
7'3"					16	19	
7'6"						36	
7'9"						17	20
8'0"							38
	90-102	96-108	102-114	108-120	114-126	120-132	123-135
8'3"		22	17				
8'6"			40				
8'9"			22	19			
9'0"				42			
9'3"				24	19		
9'6"					44		
9'9"					36	9	
10'0"						46	
10'3"							48

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 125.—9-IN. ROTARY-KILN BLOCKS

Inside diameter	No. required to turn circle					
	48-66	54-72	60-78	66-84	72-90	78-96
4'0"	23					
4'3"	11	13				
4'6"		26				
4'9"		14	13			
5'0"			28			
5'3"			15	14		
5'6"				30		
5'9"				12	19	
6'0"					32	
6'3"					14	19
	72-90	78-96	84-102	90-108	96-114	102-120
6'6"		34				
6'9"		16	19			
7'0"			36			
7'3"			17	20		
7'6"				38		
7'9"				22	17	
8'0"					40	
8'3"					27	14
8'6"						42
	102-120	108-126	114-132	117-135	120-138	123-141
8'9"	25	18				
9'0"		44				
9'3"		27	18			
9'6"			46			
9'9"				48		
10'0"					49	
10'3"						50
	123-141	126-144	132-150	138-156	144-162	150-168
10'6"		51				
10'9"		14	38			
11'0"			53			
11'3"			24	30		
11'6"				55		
11'9"				34	22	
12'0"					57	
12'3"					24	34
12'6"						59

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

fully fitted and not driven in too hard; otherwise the crown will be strained and the key cracked. Insulating-firebrick keys should never be hammered into place.

6. Domes. *Stresses in Domes.*—As the stresses in domes are redundant, it is difficult to obtain an exact evaluation. The band stress, however, is approximately given by

$$\frac{\text{Total weight of dome}}{\cos \frac{1}{2}\theta}$$

or

$$\frac{2\pi r_m h_m t d}{\cos \frac{1}{2}\theta}$$

in pounds

where d = the bulk density of the refractory in lb. per cu. in. and the other symbols are shown in Fig. 403.

It should be noted that in the same way as for the cylindrical roof, the spherical dome is not the most stable form. Fellows⁽³⁾ and Goodier^(3a) have shown that this limiting form approaches the surface of revolution formed by an ellipse. Any dome *inside* this surface is stable.

Brickwork Estimating.—The dome can be constructed of radial blocks with a double taper to fit the particular radius used, or it can be made out of standard shapes such as straights, wedges, and keys, as is the usual practice in kiln construction. It will be seen, however, that perfect fitting cannot be obtained in either case and mortar must be used to make up the difference. The estimation of brick for the dome is a little complicated, but the following method will probably be found satisfactory for most cases.

With the Use of Special Blocks.—The spherical dome can be best constructed of special shapes having a large end of $4\frac{1}{2}$ by $2\frac{1}{2}$ in. and a taper such that a projection of their corners will pass through the center of curvature of the dome. This allows strictly radial joints, and either $2\frac{1}{2}$ - or $4\frac{1}{2}$ -in. rings. However, as the rings approach the top of the crown, even these blocks will not fit perfectly unless hand cut. In practice, such shapes can be economically made by grinding insulating firebrick, but with heavy bricks this is not generally feasible. Table 126 gives the dimensions of the small end of the bricks for 9 in. thick domes having various radii of curvature.

TABLE 126.—RADIAL DOME BRICK

Size of dome, radius of curvature (inside surface)	Size of inner ends	
	Width, in.	Thickness, in.
4 ft. = 48 in.	3.79	2.11
6 ft. = 72 in.	4.00	2.22
8 ft. = 96 in.	4.12	2.29
10 ft. = 120 in.	4.18	2.33
14 ft. = 168 in.	4.28	2.37
18 ft. = 226 in.	4.33	2.40
24 ft. = 288 in.	4.36	2.42
30 ft. = 360 in.	4.39	2.44
40 ft. = 480 in.	4.42	2.45

With the Use of Standard Shapes.—Most domes are built up in 2½-in. rings with combinations of straights and keys alternated with 4½-in. rings of straights and wedges to give the curvature in both directions. A by no means accurate fit can be obtained,

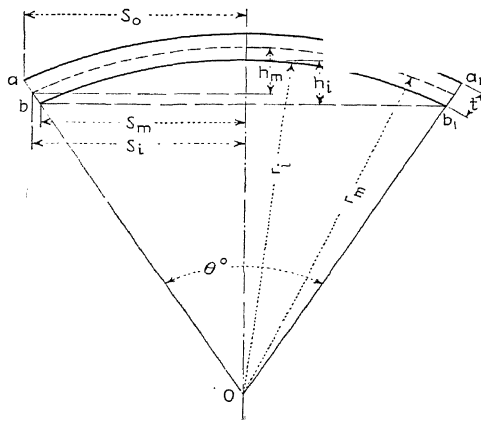


FIG. 403.—Section of a dome.

and mortar must be used to fill the joints. The estimation of the brickwork has been rather empirical, but the following method will give fairly close results.

Referring to Fig. 403, where a cross section of a typical dome is shown, the following relations are evident, all dimensions being

in inches. It is assumed, as in the usual construction, that all the rings are $2\frac{1}{2}$ in. wide.

The area of the outer surface of the dome

$$A = 2\pi(r_m + \frac{1}{2}t)h_m$$

Where h_m = the rise = $r_m - \sqrt{r_m^2 - s_m^2}$

The circumference of the segment at $a = 2\pi\left(r_m + \frac{1}{2}t\right) \cdot \sin \frac{1}{2}\theta$

The circumference of the segment at $b = 2\pi\left(r_m - \frac{1}{2}t\right) \cdot \sin \frac{1}{2}\theta$

$\frac{\text{Circumference at } a}{4.5}$ = number of 9-in. equivalents in first ring.

$\frac{\text{Circumference at } a - \text{circumference at } b}{4.5 - 4.0}$ = number of No. 1 keys in first ring

$$\text{Arc } aa_1 = 2\pi\left(r_m + \frac{1}{2}t\right) \frac{\theta}{360}$$

$$\text{Arc } bb_1 = 2\pi\left(r_m - \frac{1}{2}t\right) \frac{\theta}{360}$$

$$\frac{aa_1}{2.5} = \text{number of rings}$$

$$\frac{aa_1 - bb_1}{2.50 - 1.88} = \text{number of No. 1 wedge rings}$$

The total number of 9-in. equivalents in the dome

$$= \frac{A}{4.5 \times 2.5} = \frac{A}{11.25}$$

Of these $\frac{(aa_1 - bb_1)/(2.50 - 1.88)}{aa_1/2.5}$ are No. 1 wedges.

The remainder have $\frac{\text{circumference at } a - \text{circumference at } b}{4.50 - 4.0}$
 $\frac{\text{circumference } a}{4.5}$

No. 1 keys and the rest are straights.

Example of Dome Calculations:

Assume $r_i = 120$ in.

$t = 9$ in.

$\theta = 60$ deg.

Circumference of segment at $a = 2\pi(129) \cdot \frac{1}{2} = 406$ in.

Circumference of segment at $b = 2\pi(120) \cdot \frac{1}{2} = 377$ in.

$$\frac{406}{4.5} = 90 \text{ nine-inch equivalents in first ring}$$

$$\frac{406 - 377}{4.5 - 4.0} = \frac{29}{0.5} = 58 \text{ No. 1 keys in first ring}$$

$$\frac{aa_1}{2.5} = \frac{129 \times 2\pi\frac{1}{6}}{2.5} = 54 \text{ rings}$$

$$\begin{aligned} \frac{aa_1 - bb_1}{2.50 - 1.88} &= \frac{129 \times 2\pi\frac{1}{6} - 120 \times 2\pi\frac{1}{6}}{0.62} = \frac{135.2 - 125.9}{0.62} \\ &= \frac{9.3}{0.62} = 15 \text{ No. 1 wedge rings} \end{aligned}$$

$$\text{Total number of brick} = \frac{2\pi 129 \times 17}{2\frac{1}{2} \times 4\frac{1}{2}} = 1,230 \text{ nine-inch equivalents in whole dome}$$

$$1,230 \times \frac{15.4}{100} = 338 \text{ No. 1 wedges}$$

$$(1,230 - 338) \frac{58}{100} = 542 \text{ No. 1 keys}$$

$$1,230 - 880 = 350 \text{ straights}$$

Domes can be constructed with $4\frac{1}{2}$ -in. rings, which are sometimes favored for movable structures like covers. The calcula-

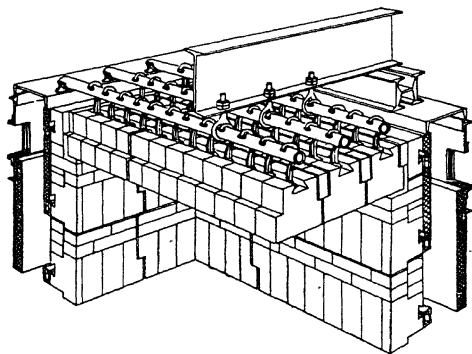


FIG. 404.—Typical suspended-arch construction. Reintjes, each tile individually supported and removable. (Courtesy of Power Magazine.)

tion can be carried out in the same way. As each ring in the dome is self-supporting, a complete form is not needed.

Steelwork.—The dome is particularly easy to brace because a simple tension band around the base will take care of the stresses

completely. The section of this band can be easily computed from the formulas previously given, allowing a factor of safety of at least 5 to take care of the elevated temperatures, corrosion, and scaling.

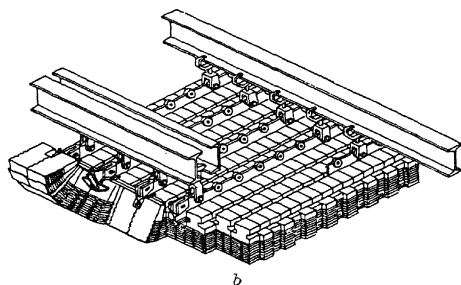


FIG. 404.—Detrick tile corrugated on all sides prevent spalled refractory from falling into furnace.

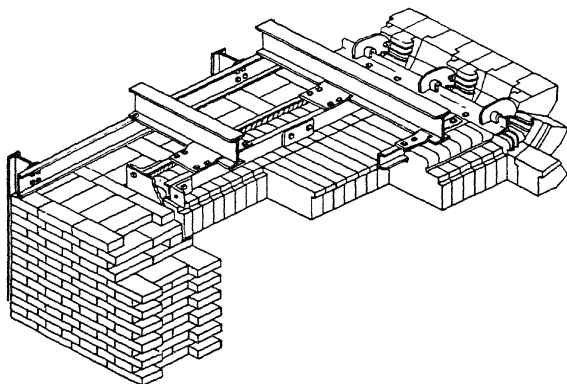


FIG. 404.—American arch, alternate rows of tile removable without disturbing channel suspension.

7. Suspended Arches. *Firebrick Suspended Arches.*—Suspended arches consist of a type of construction where individual refractory units are held in place by a metal support tied to an overhead framework. In this type of arch, a single unit can be replaced without disturbing the whole crown. There are a great many types of block used for constructing these arches,

some of the best known being shown in Fig. 404. This type of construction is useful for flat or special shaped roofs. It also allows an unlimited width. However, it cannot be insulated so completely as the sprung arch and is somewhat more costly.

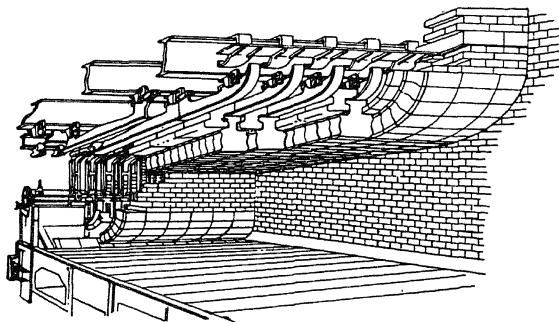


FIG. 404.—Bigelow-Liptak, double suspensions increase refractory that can be eroded.

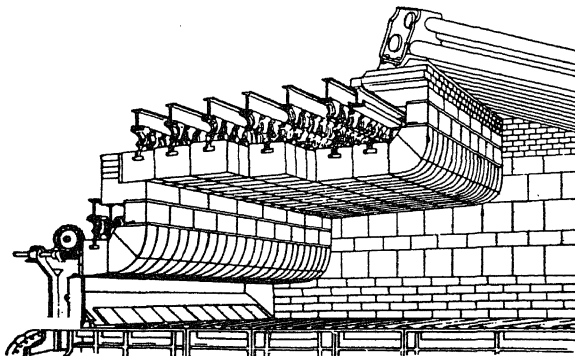


FIG. 404.—McLeod & Henry, each tile individually supported and removable.

Insulating-firebrick Suspended Arches.—Insulating firebrick are particularly adapted to use in suspended arches because they are light in weight and thus permit an inexpensive supporting framework. Two typical types of suspended arch developed by the Babcock and Wilcox Company are shown in Fig. 405, where the

brick units are threaded on light steel or alloy rods and supported on light steel hangers. Such a roof is comparatively inexpensive

Recesses in bricks at all hanger locations

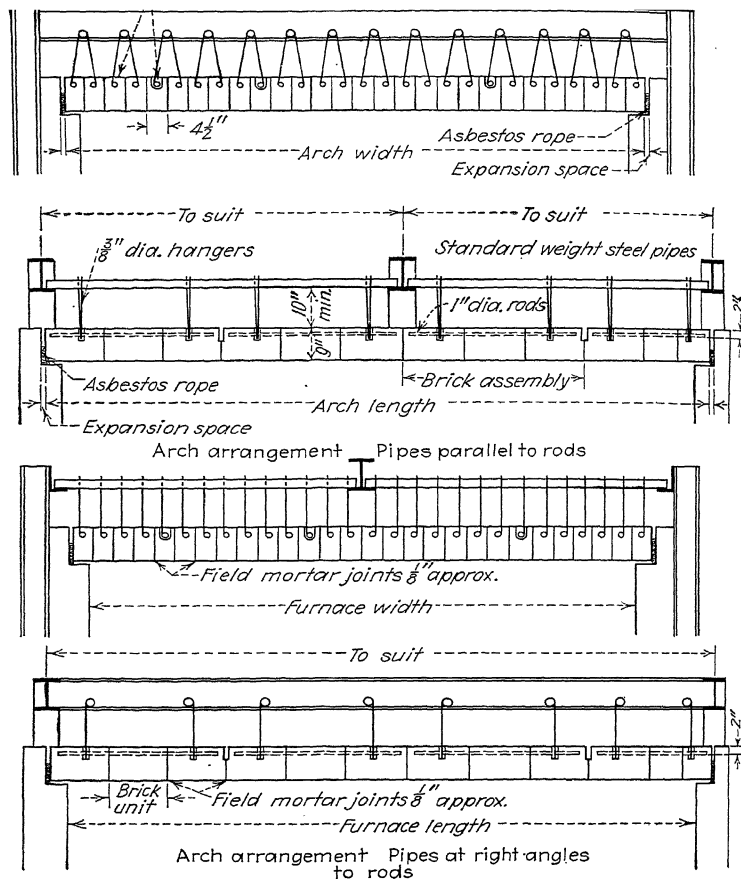


FIG. 405.—Arrangement of Babcock & Wilcox insulating firebrick for 9-in. flat suspended arches. (Courtesy of Babcock and Wilcox Company.)

to set up and generally gives excellent service. This type of construction is used a great deal in the larger heat-treating

furnaces and oil stills because there is no limit to the span that can be obtained. It also finds application in soaking pit covers where the light weight allows rapid action.

In this type of roof, 9-in. straights can be used which are easy to drill and assemble. The high insulating value of the insulating firebrick keeps the supporting steelwork comparatively cool. Usually the whole roof, even when as large as 20 by 20 ft., is cemented together with air-set mortar into a monolithic structure with the only expansion joint around the edge. This joint should be sealed for gas tightness.

8. Brick Laying.—It is needless to say that good refractory construction requires the services of an experienced furnace-brick mason. Even under these conditions, complete drawings should be prepared for anything except the simplest structures. Joints should be kept thin, which is possible with modern refractories of uniform size.

As to the cost of brick laying, it is hard to give any definite figure because of the variation in wages. In a general way, the cost of labor may be \$50 per thousand on small jobs, depending, of course, on the amount of cutting. However, the brick contractor will have to add to the cost of labor, refractories, and mortar items such as hauling materials and tools, insurance, and old-age pensions, as well as overhead and profit. On small jobs, \$75 to \$100 per thousand should be allowed for laying costs in addition to the cost of the refractories; but on large jobs like an open-hearth furnace, \$40 to \$50 might cover the laying costs.

When ordering brick, a certain amount in addition to that estimated must be added for losses in cutting, broken bricks, etc. This is called "overage" and amounts to from 2 to 5 per cent on large jobs to 10 or 15 per cent on small ones. If there is much cutting, the overage must be increased. It also should be remembered that when bricks come in cartons, the number ordered must be an even multiple of the number in the carton, which may make it necessary to purchase more bricks than actually needed.

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APPENDIX

Reference Tables

TABLE 127.—TEMPERATURE-CONVERSION TABLE
(Dr. L. Waldo, in *Metallurgical and Chemical Engineering*, March, 1910)

C	0	10	20	30	40	50	60	70	80	90		
	F	F	F	F	F	F	F	F	F	F		
-200	-328	-348	-364	-382	-400	-418	-436	-454	-472	-490		
-100	-148	-166	-184	-202	-220	-238	-256	-274	-292	-310		
0	+ 32	+ 14	- 4	- 22	- 40	- 58	- 76	- 94	- 112	- 130		
0	32	50	68	86	104	122	140	158	176	194	°C.	°F.
100	212	230	248	266	284	302	320	338	356	374	1	1.8
200	392	410	428	446	464	482	500	518	536	554	2	3.6
300	572	590	608	626	644	662	680	698	716	734	3	5.4
400	752	770	788	806	824	842	860	878	896	914	4	7.2
500	932	950	968	986	1004	1022	1040	1058	1076	1094	5	9.0
600	1112	1130	1148	1166	1184	1202	1220	1238	1256	1274	6	10.8
700	1292	1310	1328	1346	1364	1382	1400	1418	1436	1454	7	12.6
800	1472	1490	1508	1526	1544	1562	1580	1598	1616	1634	8	14.4
900	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814	9	16.2
1000	1832	1850	1868	1886	1904	1922	1940	1958	1976	1994	10	18.0
1100	2012	2030	2048	2066	2084	2102	2120	2138	2156	2174		
1200	2192	2210	2228	2246	2264	2282	2300	2318	2336	2354	°F.	°C.
1300	2372	2390	2408	2426	2444	2462	2480	2498	2516	2534		
1400	2552	2570	2588	2606	2624	2642	2660	2678	2696	2714	1	0.56
1500	2732	2750	2768	2786	2804	2822	2840	2858	2876	2894	2	1.11
1600	2912	2930	2948	2966	2984	3002	3020	3038	3056	3074	3	1.67
1700	3092	3110	3128	3146	3164	3182	3200	3218	3236	3254	4	2.22
1800	3272	3290	3308	3326	3344	3362	3380	3398	3416	3434	5	2.78
1900	3452	3470	3488	3506	3524	3542	3560	3578	3596	3614	6	3.33
2000	3632	3650	3668	3686	3704	3722	3740	3758	3776	3794	7	3.89
2100	3812	3830	3848	3866	3884	3902	3920	3938	3956	3974	8	4.44
2200	3992	4010	4028	4046	4064	4082	4100	4118	4136	4154	9	5.00
2300	4172	4190	4208	4226	4244	4262	4280	4298	4316	4334	10	5.56
2400	4352	4370	4388	4406	4424	4442	4460	4478	4496	4514	11	6.11
2500	4532	4550	4568	4586	4604	4622	4640	4658	4676	4694	12	6.67
2600	4712	4730	4748	4766	4784	4802	4820	4838	4856	4874	13	7.22
2700	4892	4910	4928	4946	4964	4982	5000	5018	5036	5054	14	7.78
2800	5072	5090	5108	5126	5144	5162	5180	5198	5216	5234	15	8.33
2900	5252	5270	5288	5306	5324	5342	5360	5378	5396	5414	16	8.89
3000	5432	5450	5468	5486	5504	5522	5540	5558	5576	5594	17	9.44
3100	5612	5630	5648	5666	5684	5702	5720	5738	5756	5774	18	10.00
3200	5792	5810	5828	5846	5864	5882	5900	5918	5936	5954		
3300	5972	5990	6008	6026	6044	6062	6080	6098	6116	6134		
3400	6152	6170	6188	6206	6224	6242	6260	6278	6296	6314		
3500	6332	6350	6368	6386	6404	6422	6440	6458	6476	6494		
3600	6512	6530	6548	6566	6584	6602	6620	6638	6656	6674		
3700	6692	6710	6728	6646	6764	6782	6800	6818	6836	6854		
3800	6872	6890	6908	6926	6944	6962	6980	6998	7016	7034		
3900	7052	7070	7088	7106	7124	7142	7160	7178	7196	7214		

Examples. 1347°C. = 2444°F. + 12.6°F. = 2456.6°F.; 3367°F. = 1850°C. + 2.78°C.
1852.78°C.

TABLE 130.—STANDARD CALIBRATION DATA FOR CHROMEL-ALUMEL COUPLES

E.m.f., millivolts	Reference junction at 32°F.					
	0	10	20	30	40	50
	Temperature, °F.					
0	32	475	905	1329	1772	2250
0.2	41	484	913	1338	1781	2260
0.4	50	493	922	1346	1790	2270
0.6	59	502	930	1355	1799	2280
0.8	68	510	939	1363	1808	2290
1.0	77	519	947	1372	1818	2300
1.2	86	528	956	1380	1827	2310
1.4	95	537	964	1389	1836	2320
1.6	104	546	973	1398	1845	2331
1.8	113	554	981	1407	1855	2341
2.0	121	563	990	1415	1864	2351
2.2	130	572	998	1424	1873	2362
2.4	139	580	1006	1433	1882	2372
2.6	147	589	1015	1441	1892	2382
2.8	156	598	1023	1450	1901	2393
3.0	165	607	1032	1459	1911	2403
3.2	173	615	1040	1467	1920	2413
3.4	182	624	1049	1476	1930	2424
3.6	190	632	1057	1485	1939	2434
3.8	199	641	1065	1494	1949	2445
4.0	208	650	1074	1503	1958	2455
4.2	217	658	1083	1511	1967	2466
4.4	225	667	1091	1520	1977	2476
4.6	234	675	1099	1529	1986	2487
4.8	243	684	1108	1538	1996	2497
5.0	251	693	1116	1547	2005	
5.2	260	701	1125	1555	2015	
5.4	269	710	1133	1564	2024	
5.6	278	718	1142	1573	2034	
5.8	287	727	1150	1582	2044	
6.0	296	735	1158	1591	2053	
6.2	305	744	1167	1600	2063	
6.4	314	752	1175	1609	2072	
6.6	323	760	1184	1618	2082	
6.8	332	769	1193	1627	2092	
7.0	341	778	1201	1636	2101	
7.2	350	786	1210	1645	2111	
7.4	359	795	1218	1654	2121	
7.6	368	803	1227	1663	2130	
7.8	377	812	1235	1672	2140	
8.0	386	820	1243	1680	2150	
8.2	395	829	1252	1689	2160	
8.4	404	838	1260	1698	2170	
8.6	413	846	1269	1708	2180	
8.8	422	855	1278	1717	2190	
9.0	431	863	1286	1726	2200	
9.2	440	872	1295	1735	2210	
9.4	449	880	1303	1744	2220	
9.6	457	889	1312	1753	2230	
9.8	466	897	1320	1762	2240	
10.0	475	905	1329	1772	2250	

TABLE 131.—STANDARD CALIBRATION DATA FOR THERMOCOUPLES FROM PLATINUM AND PLATINUM ALLOYED WITH 10 PER CENT RHODIUM

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °C.									
0	0.0	147.1	265.4	374.3	478.1	578.3	675.3	769.5	861.1	950.4
100	17.8	159.7	276.6	384.9	488.3	588.1	684.8	778.8	870.1	959.2
200	34.5	172.1	287.7	395.4	498.4	597.9	694.3	788.0	879.1	968.0
300	50.3	184.3	298.7	405.9	508.5	607.7	703.8	797.2	888.1	976.7
400	65.4	196.3	309.7	416.3	518.6	617.4	713.3	806.4	897.1	985.4
500	80.0	208.1	320.6	426.7	528.6	627.1	722.7	815.6	906.1	994.1
600	94.1	219.7	331.5	437.1	538.6	636.8	732.1	824.7	915.0	1002.8
700	107.8	231.2	342.3	447.4	548.6	646.5	741.5	833.8	923.9	1011.5
800	121.2	242.7	353.0	457.7	558.5	656.1	750.9	842.9	932.8	1020.1
900	134.3	254.1	363.7	467.9	568.4	665.7	760.2	852.0	941.6	1028.7
1,000	147.1	265.4	374.3	478.1	578.3	675.3	769.5	861.1	950.4	1037.3

E.m.f., microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000
	Temperatures °C.								
0	1037.3	1122.2	1205.9	1289.3	1372.4	1454.8	1537.5	1620.9	1704.3
100	1045.9	1130.6	1214.2	1297.7	1380.7	1463.0	1545.8	1629.2	1712.6
200	1054.4	1139.0	1222.6	1306.0	1389.0	1471.2	1554.1	1637.6	1721.0
300	1062.9	1147.4	1230.9	1314.3	1397.3	1479.4	1562.4	1645.9	1729.3
400	1071.4	1155.8	1239.3	1322.6	1405.6	1487.7	1570.8	1654.3	1737.7
500	1079.9	1164.2	1247.6	1330.9	1413.8	1496.0	1579.1	1662.6	1746.0
600	1088.4	1172.5	1255.9	1339.2	1422.0	1504.3	1587.5	1670.9	1754.3
700	1096.9	1180.9	1264.3	1347.5	1430.2	1512.6	1595.8	1679.3	
800	1105.4	1189.2	1272.6	1355.8	1438.4	1520.9	1604.2	1687.6	
900	1113.8	1197.6	1281.0	1364.1	1446.6	1529.2	1612.5	1696.0	
1,000	1122.2	1205.9	1289.3	1372.4	1454.8	1537.5	1620.9	1704.3	

TABLE 132.—STANDARD CALIBRATION DATA FOR THERMOCOUPLES FROM PLATINUM AND PLATINUM ALLOYED WITH 10 PER CENT RHODIUM

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °F.									
0	32.0	296.8	509.7	705.7	892.6	1072.9	1247.5	1417.1	1582.0	1742.7
100	42.0	319.5	529.9	724.8	910.9	1090.6	1264.6	1433.8	1598.2	1758.6
200	94.1	341.8	549.9	743.7	929.1	1108.2	1281.7	1450.4	1614.4	1774.4
300	122.5	363.7	569.7	762.6	947.3	1125.9	1298.8	1467.0	1630.6	1790.1
400	149.7	385.3	589.5	781.3	965.5	1143.3	1315.9	1483.5	1646.8	1805.7
500	176.0	406.6	609.1	800.1	983.5	1160.8	1332.9	1500.1	1663.0	1821.4
600	201.4	427.5	628.7	818.8	1001.5	1178.2	1349.8	1516.5	1679.0	1837.0
700	226.0	448.2	648.1	837.3	1019.5	1195.7	1366.7	1532.8	1694.8	1852.7
800	250.2	468.9	667.4	855.9	1037.3	1213.0	1383.6	1549.2	1711.0	1868.2
900	273.7	489.4	686.7	874.2	1055.1	1230.3	1400.4	1565.6	1726.9	1883.7
1,000	296.8	509.7	705.7	892.6	1072.9	1247.5	1417.1	1582.0	1742.7	1899.1

E.m.f., microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000
	Temperatures °F.								
0	1899.1	2052.0	2202.6	2352.7	2502.3	2650.6	2799.5	2949.6	3099.7
100	1914.6	2067.1	2217.6	2367.9	2517.3	2665.4	2814.4	2964.6	3114.7
200	1929.9	2082.2	2232.7	2382.8	2532.2	2680.2	2829.4	2979.7	3129.8
300	1945.2	2097.3	2247.6	2397.7	2547.1	2694.9	2844.3	2994.6	3144.7
400	1960.5	2112.4	2262.7	2412.7	2562.1	2709.9	2859.4	3009.7	3159.9
500	1975.8	2127.6	2277.7	2427.6	2576.8	2724.8	2874.4	3024.7	3174.8
600	1991.1	2142.5	2292.6	2442.6	2591.6	2739.7	2889.5	3039.6	3189.7
700	2006.4	2157.6	2307.7	2457.5	2606.4	2754.7	2904.4	3054.7	
800	2021.7	2172.6	2322.7	2472.4	2621.1	2769.6	2919.6	3069.7	
900	2036.8	2187.7	2337.8	2487.4	2635.9	2784.6	2934.5	3084.8	
1,000	2052.0	2202.6	2352.7	2502.3	2650.6	2799.5	2949.6	3099.7	

TABLE 133.—STANDARD CALIBRATION DATA FOR COPPER-CONSTANTAN THERMOCOUPLE

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °C.									
0	0.0	25.3	49.2	72.1	94.1	115.3	135.9	155.9	175.5	194.6
100	2.6	27.7	51.5	74.3	96.2	117.4	137.9	157.0	177.4	196.5
200	5.2	30.2	53.9	76.5	98.4	119.5	140.0	159.9	179.4	198.4
300	7.7	32.6	56.2	78.8	100.5	121.6	142.0	161.9	181.3	200.3
400	10.3	35.0	58.5	81.0	102.7	123.6	144.0	163.8	183.2	202.2
500	12.8	37.4	60.8	83.2	104.8	125.7	146.0	165.8	185.1	204.0
600	15.3	39.8	63.0	85.4	106.9	127.7	148.0	167.7	187.0	205.9
700	17.8	42.2	65.3	87.6	109.0	129.8	150.0	169.7	188.0	207.8
800	20.3	44.5	67.6	89.7	111.1	131.8	152.0	171.6	190.8	209.8
900	22.8	46.9	69.8	91.9	113.2	133.9	154.0	173.6	192.7	211.5
1,000	25.3	49.2	72.1	94.1	115.3	135.9	155.9	175.5	194.6	213.4

10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000
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Temperatures °C.

0	213.4	231.7	249.8	267.6	285.1	302.4	319.5	336.4	353.1
100	215.2	233.6	251.6	269.4	286.9	304.1	321.2	338.0	
200	217.2	235.4	253.4	271.1	288.6	305.9	322.9	339.7	
300	218.9	237.2	255.2	272.9	290.3	307.6	324.6	341.4	
400	220.8	239.0	257.0	274.6	292.1	309.3	326.3	343.1	
500	222.6	240.8	258.7	276.4	293.8	311.0	327.9	344.7	
600	224.4	242.6	260.5	278.2	295.5	312.7	329.6	346.4	
700	226.3	244.4	262.3	279.9	297.3	314.4	331.3	348.1	
800	228.1	246.2	264.1	281.6	299.0	316.1	333.0	349.7	
900	229.9	248.0	265.8	283.4	300.7	317.8	334.7	351.4	
1,000	231.7	249.8	267.6	285.1	302.4	319.5	336.4	353.1	

TABLE 134.—STANDARD CALIBRATION DATA FOR COPPER-CONSTANTAN THERMOCOUPLE

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °F.									
0	32.0	77.5	120.6	161.7	201.3	239.6	276.6	312.7	347.9	382.3
100	36.7	81.9	124.8	165.7	205.2	243.3	280.3	314.6	351.4	385.7
200	41.4	86.3	128.9	169.8	209.1	247.1	283.9	319.8	354.8	389.1
300	45.9	90.6	133.1	173.9	212.9	250.8	287.6	323.3	358.3	392.5
400	50.5	95.0	137.2	177.7	216.8	254.5	291.2	326.9	361.8	395.9
500	55.0	99.3	141.4	181.7	220.6	258.2	294.8	330.4	365.2	399.3
600	59.5	103.6	145.5	185.7	224.4	261.9	298.4	333.9	368.6	402.6
700	64.0	107.9	149.5	189.6	228.2	265.6	302.0	337.4	370.4	406.0
800	68.5	112.1	153.6	193.5	232.0	269.3	305.6	340.9	375.6	409.3
900	73.0	116.3	157.7	197.4	235.8	273.0	309.1	344.4	378.9	412.7
1,000	77.5	120.6	161.7	201.3	239.6	276.6	312.7	347.9	382.3	416.0

E.m.f., microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000	19,000
	Temperatures °F.									
0	416.0	449.1	481.7	513.7	545.2	576.4	607.1	637.4	667.6	
100	419.4	452.4	484.9	516.8	548.4	579.4	610.1	640.5		
200	423.0	455.7	488.1	519.0	551.5	582.5	613.2	643.5		
300	426.0	459.0	491.3	523.2	554.6	585.6	616.2	646.5		
400	429.3	462.2	494.5	526.4	557.7	588.7	619.3	649.5		
500	432.7	465.5	497.7	529.5	560.8	591.8	622.3	652.5		
600	436.0	468.7	500.9	532.7	564.0	594.8	625.4	655.5		
700	439.3	472.0	504.1	535.8	567.1	597.9	628.4	658.5		
800	442.6	475.2	507.3	539.0	570.2	601.0	631.4	661.6		
900	445.9	478.4	510.5	542.1	573.6	604.0	634.4	664.6		
1,000	449.1	481.7	513.7	545.2	576.4	607.1	637.4	667.6		

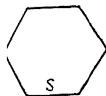
TABLE 135.—FORMULAS USEFUL IN CALCULATIONS

*Rectangle:*

$$\text{Area} = ab$$

*Triangle:*

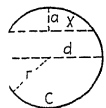
$$\text{Area} = \frac{ah}{2}$$

Regular Polygon:

Sides	Area
5	$1.720 \times S^2$
6	$2.598 \times S^2$
7	$3.634 \times S^2$
8	$4.828 \times S^2$
9	$6.182 \times S^2$
10	$7.694 \times S^2$
11	$9.366 \times S^2$
12	$11.196 \times S^2$

Circle:

$$\text{Circumference} = \pi d = 2\pi r$$



$$\text{Diameter} = 2r = \frac{C}{\pi} = 2 \sqrt{\frac{\text{area}}{\pi}}$$

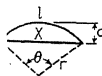
$$\text{Radius} = \frac{d}{2} = \frac{C}{2\pi} = \sqrt{\frac{\text{area}}{\pi}}$$

$$\text{Area} = \frac{\pi d^2}{4} = \pi r^2 = 0.7854d^2$$

$$\text{Length of chord, } x = 2 \sqrt{a(d-a)} = 2r(\sin \frac{1}{2}\theta)$$

Segment:

$$\text{Area} = \frac{rl - x(r-a)}{2}$$



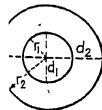
$$\text{Height of arc above chord, } u = r - \sqrt{r^2 - \left(\frac{x}{2}\right)^2}$$

$$\text{Radius, when chord and height are known, } r = \frac{\left(\frac{x}{2}\right)^2 + h^2}{2h}$$

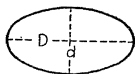
$$\text{Length of arc, } l = 2\pi r \frac{\theta}{360} = \pi r \frac{\theta}{180}$$

Sector:

$$\text{Area} = \frac{1}{2} lr = \pi r^2 \frac{\theta}{360}$$

*Annulus (Circular Ring):*

$$\begin{aligned} \text{Area} &= \pi(r_2^2 - r_1^2) \\ &= \pi(r_2 + r_1)(r_2 - r_1) \\ &= 0.7854(d_2^2 - d_1^2) \end{aligned}$$

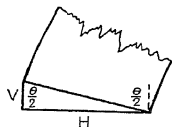
Ellipse:

$$\text{Area} = \frac{\pi}{4} Dd \quad 0.7854Dd$$

$$\text{Perimeter (approx.)} = 2\pi \sqrt{\frac{D^2 + d^2}{8}}$$

Skewbacks:

To find a skew to fit a given arch:

1. Find subtended angle θ 2. Find sine and cosine of $\frac{1}{2}\theta$ 3. H = thickness of arch $\times \sin \frac{1}{2}\theta$ 4. V = thickness of arch $\times \cos \frac{1}{2}\theta$ Slope of the skewback from the horizontal = $90^\circ - \frac{1}{2}\theta$ *Circle Brick:*

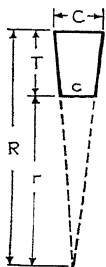
$$\text{Radius of radial brick, } r = \frac{cT}{(C - c)}$$

Number of radial brick to make a circle:

$$n = \frac{\pi \times \text{diameter of circle}}{\text{thickness of large end}} \\ = \frac{2\pi r}{C}$$

Number of straights to fill out a circle of given diameter using given number of radial brick:

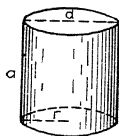
$$n = \frac{\pi(\text{given outside diameter}) - (\text{possible diameter with radial brick})}{\text{thickness of straight}}$$

*Cylinder:*

$$\text{Volume} = \pi r^2 a \\ = 0.7854 d^2 a$$

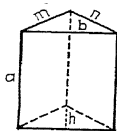
$$\text{Cylindrical surface area} = \pi da$$

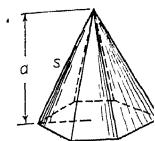
$$\text{Total surface area} = 2\pi r(r + a)$$

*Regular Triangular Prisms:*

$$\text{Volume} = \frac{1}{2}bha$$

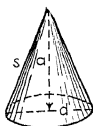
$$\text{Lateral surface area} = (b + m + n)a$$



*Pyramid:*

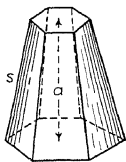
$$\text{Volume} = \text{area of base} \times a$$

$$\text{Lateral surface area} = \frac{\text{perimeter of base} \times s}{2}$$

*Cone:*

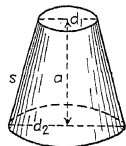
$$\begin{aligned} \text{Volume} &= \frac{\pi r^2 a}{3} \\ &= 0.2618 d^2 a \end{aligned}$$

$$\text{Lateral surface area} = \pi r s$$

*Frustum of Pyramid:*

$$\text{Lateral surface area} = \frac{(P + p)s}{2}$$

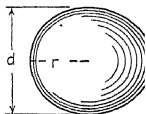
$$\text{Volume} = \frac{a}{3} (b + B + \sqrt{Bb})$$

where P = perimeter of lower base p = perimeter of upper base B = area of lower base b = area of upper base*Frustum of Cone:*

$$\text{Volume} = \frac{a}{3} (b + B + \sqrt{Bb}), \text{ or}$$

$$= \frac{\pi}{12} a (d_1^2 + d_1 d_2 + d_2^2)$$

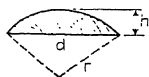
$$\text{Area of conic surface} = \frac{\pi S}{2} (d_1 + d_2)$$

*Sphere:*

$$\text{Area of surface} = 4\pi r^2 = \pi d^2 = 12.566r^2$$

$$\text{Volume} = \frac{4\pi r^3}{3} = 4.1888r^3$$

$$= \frac{\pi}{6} d^3 = 0.5236d^3$$

*Segment of Sphere:*

$$\text{Area of spherical surface} = 2\pi r h = \frac{\pi}{4} (d^2 + 4h^2)$$

$$\text{Volume} = \pi h^2 \left(r - \frac{h}{3} \right)$$



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